Chem Ed

EDITORIALLY SPEAKING

Whose Division? Every Member's!

The universal comment heard in the crowded lobbies of Cleveland hotels during the recent ACS meeting was, "That was a terrific symposium. The Division of Chemical Education certainly is on the ball." Standing-room-only audiences were enthusiastic in their appreciation of the well-coordinated series of outstanding papers. This enthusiasm is all the more tribute to those who planned the programs and to the speakers themselves because of the inadequate audio and visual equipment which was provided. "New Outlooks in Organic Chemistry," "Recent Advances in Inorganic Chemistry" and "Geochemistry" were a series that will long be remembered.

Much goes into successful program planning by the Division's imaginative and hard-working program committee. Themes are chosen years in advance. Willing and well-informed symposium chairmen plan far ahead to coordinate topics and invite outstanding authorities to present the papers. One especially commendable feature of the Cleveland programs was that each speaker was allowed sufficient time to deal adequately with his subject and to answer questions. ACS members should be grateful to the many who made possible this means of becoming well-informed on the present status of rapidly advancing knowledge.

There was, however, one disturbing aspect of the Division of Chemical Education program at Cleveland. This was the small number of uninvited papers submitted for the general session. Certainly none could claim that the meager program of seven papers lacked quality, timeliness, nor general interest. The unfortunate feature of the session was its enforced heterogeneity. The virtual impossiblity of scheduling an afternoon of travel between hotels to hear one or two papers in various sessions means that potential listeners often are forced to miss an isolated paper of particular interest. The absence of these individuals from the audience and the consequent paucity of discussion is disappointing, if not discouraging, to the speaker. The purpose of the general session is to give chemistry teachers an opportunity to share ideas and enthusiasms and to submit them to the scrutiny of open discussion for evaluation. A circumstance which prevents fulfilling this purpose is unfortunate and should be corrected.

The success of the general program is the concern and obligation of every member of the Division. There certainly is no dearth of new ideas constantly being injected into chemistry teaching. The utility of some of these may be questioned, but no potential contributor should prejudge either his topic as inconsequential or his audience as hypercritical. (It should be pointed out, however, lest the impression be given that submission guarantees a place on the program, that the program committee reserves the right to exercise critical judgment and to reject some papers as inappropriate.) Division members collectively need a strong program of submitted papers. Ideas always catalyze other ideas and discussion invariably refines them.

New techniques of presenting the material in conventional courses is grist to the mill of good chemistry teaching. Curriculum planning, both within the conventional framework and innovations in organization of new courses, always attracts attention and calls for discussion. Laboratory experiments are another subject appropriate for papers that share experiences. Demonstrations may be difficult to perform in a hotel ballroom, but at least their description is always welcome.

The value of a general meeting is the quick dissemination of knowledge and the exchange of both experience and conjecture on a personal level. The Division's program will fulfill this function for those in attendance only if its program is strong. Presenting papers is more than a privilege, it is an obligation. We urge members whose ideas have increased the yield in their teaching this past year to plan to tell others about it at the New York meeting in September. Two copies of the manuscript or a 1000-word abstract along with three copies of a 250-word abstract should be sent to Professor Clark E. Bricker at Princeton University (N. J.). The deadline is June 6, 1960.

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Use of Metal Complexes in Organic Dyes and Pigments

One of the most fascinating aspects of modern organic chemistry and related natural sciences is the ever-increasing academic and commercial interest enjoyed by organic metal complexes. Significantly, they have become important particularly in the branches of biology, catalysis, analytical chemistry, and in the technology of organic dyes and pigments, where the most spectacular progress was made during the last two decades. This paper summarizes some of the historical, theoretical, and commercial aspects of the use being made of metal complexes in man-made organic dyes and pigments, touching only briefly (from an historical viewpoint) on metal complexes or lakes made from natural coloring products.

Metal Complexes of Natural Dyes

The origin of metallized organic dyes and pigments is lost in antiquity. We know that highly insoluble combinations of such natural coloring materials as Brazilwood, logwood, kermes, lac-dye, cochineal, Persian berries, and especially madder with crude clay-like materials were prepared by ancient people in substance or *in situ* for decorative purposes. Thousands of years ago it must have been observed that this complexing or "laking" of most of the then available natural coloring materials with clay-like diluents or extenders markedly increased the intensity and fastness of the dyeings on fabric, and produced insoluble pigments. In fact, the name "lake" is derived from the Sanskrit *Laksha*, meaning a hundred thousand and thus associates one of these prehistoric pigments with the insect lucifer lacca, which furnished the "lac-dye." This natural dye was used in combination with clayey materials for the dyeing of fabric and also for producing in substance a pigment which was incorporated into oily and resinous vehicles. The most important of the natural dyes capable of forming metal complexes is madder. Having first been used in India, this excellent textile dye, and the strong and bright red pigment derived therefrom, appear to have been known equally well to the ancient Persians and Egyptians as it was much later to the Greeks and Romans. Madder-dyed cloth has been found on Egyptian mummies in tombs of a predynastic era; Herodotus reported about 450 B.C. that Libyan women used this dye to "brighten their cloaks" (*1*). Madder probably was the red dye which enabled Alexander the Great 120 years later to win a decisive battle against a much larger Persian army, when the latter at daybreak on the second day of fighting, recklessly rushed in for the kill. Surely, here was their chance to finish off an invader whose soldiers had become so completely demoralized by the fighting of the previous day that their many seriously wounded comrades had not even received medical attention during the night. In their ill-advised dreaming of an easy victory, it did not occur to them that this was the first recorded use of camouflage in war, conceived by the cunning Alexander who had purchased the red dye from native craftsmen skilled in the art of dyeing cloth with madder (*2*) and had dyed the clothing of most of his men with large, blood-like spots, each at a different location on the garment.

Until the advent of the synthetic dyes from coal tar intermediates, madder was cultivated throughout the world; in Europe it reigned supreme for centuries as the best red available for the dying of woolen and cotton fabric which had been mordanted with alum. The term mordant, derived from the Latin word *mordere* (to bite or corrode), was coined by the early French dyers who believed that the sulfuric acid in the conventional mordant acted to "corrode" or open up the fibers, thus making them receptive for dyeing with madder. In a temporarily successful attempt to succor the declining home industry, King Louis Philippe ordered in 1840 that the trousers and caps of the entire French army be dyed red with madder. The famous "Red Coats" of the British army, and the coats worn by all participants in the royal sport of fox hunting, also were dyed with madder in accordance with a decree issued by King Henry II (*3*).

From madder the highly valued pigment known as "Turkey Red Lake"[1] was produced by a tedious procedure involving boiling of the commercial dye with alumina hydrate, in the presence of calcium salts and "Turkey Red Oil,"[1] a sulfated castor oil.

Today we know that dyeing with madder is based on forming *in situ* a six-membered, cyclic chelate involving the metal (usually aluminum) and the alpha-hydroxy oxygen together with the nearest keto oxygen located

—The cover—

The unusual structure shown in perspective is a solvent-soluble precursor which can be reduced *in situ* to produce a copper phthalocyanine dye. The copper in this unusual compound exhibits a coordination number of six. The portion of the molecule extending to the lower right in the drawing splits off during the reductive treatment leaving the familiar permanent structures shown in Figures 1 and 2 of the article.

Based on an informal lecture originally presented by the author on May 22, 1959, at the Cobb Chemical Laboratory, University of Virginia.

[1] The ... plained ... dyers ob... city, and ... to be dye... was a sp...

in the 9 (or 10)-position of about six different hydroxyanthraquinones, which are originally present in madder as the glucosides. As the most prominent of these coloring components Robiquet and Colin in 1826 isolated alizarin, which is 1,2-dihydroxyanthraquinone, the dye classified in the Colour Index as Mordant Red 11 (C.I. 58000), first synthesized in 1868 by Graebe and Liebermann (*4*) by treating dibromoanthraquinone with potassium hydroxide.

The structure of the highly stable 4:2:3 alizarin:aluminum:calcium complex now produced as Turkey Red Lake, C. I. Pigment Red 83, has been discussed by Fierz-David and Rutishauser (*68*) and by E. R. Allen in Lubs (*5*).

The attractive bluish-red shade obtained with natural madder can be approached, but not matched by dyeings with synthetic alizarin; the madder dyeing resembles a dyeing of the relatively old (1882), but still commercially important disazo dye represented by Du Pont's Crocein Scarlet N, classified as Acid Red 73 (C. I. 27290), which is made by coupling diazotized *p*-phenylazoaniline with 2-naphthol-6,8-disulfonic acid, commonly known as "G acid."

Commercial dyes and pigments are classified according to application methods (for the convenience of the dyer), and also according to their chemical structures, by judiciously assigning Colour Index numbers. The latest (1956) four-volume edition of this international index was sponsored jointly by the Society of Dyers and Colourists (England) and the American Association of Textile Chemists and Colorists. Volume 3 lists approximately 3800 individual dyes and pigments, each with structural formula, methods of preparation, major literature references, and original trade names, if commonly used in the literature. In this article the chemical classification numbers (assigned in Volume 3 of the Colour Index) are shown in parenthesis, after citing the use classification names and numbers given in the first two volumes to each commercially active color.

In addition to these international designations, each manufacturer labels his brands either with old trade names (often of German origin) or, more frequently, with registered trademarks which preferably have no meaning other than to identify his particular brand of the color. The older trade names were usually chosen to indicate some distinguishing feature, such as dyeing shade, an important fastness property, method of application, fiber for which the dye was designed, location of the first producer, some event that occurred at the time of its discovery, or a significant intermediate used in its synthesis. Thus, the name of the "Crocein" scarlet mentioned above originated with the first (1881) dye of this type, in which Crocein acid (2-naphthol-8-sulfonic acid) served as the coupling component. "Crocein" is in turn derived from the Latin *croceus*, yellow.

The letters placed after the trade name, often with preceding numbers, indicate to what extent, and in what direction, the dyeing shade obtained with the commercial product differs from an agreed reference hue.

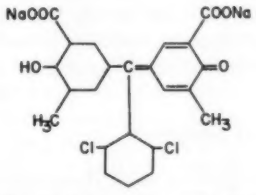
[1] The association of Turkey with these common names is explained by the apparent facts that at one time the European dyers obtained this color as "Adrianople Red" from this Turkish city, and that also the oil used at that time for pre-treating fabric to be dyed with this color, and in the preparation of the pigment, was a special grade of olive oil supplied by Turkish territories.

Metal Complexes of Synthetic Dyes and Pigments

Except for madder, metal complexes were not used to a significant extent until the advent of synthetic dyes and pigments. It then became apparent to chemists that the formation of stable metal complexes useful in dyes is contingent upon the presence of well-definable laking or complexing groups in the dye molecule. Among these, the originally utilized ortho-dihydroxy and the later available salicylic acid (*o*-hydroxycarboxy) grouping built into the molecules of anthraquinone or triphenylmethane type dyes were first exploited for application on mordanted wool. Later, just prior to the turn of the century, metallizable azo dyes became very important.

Chromable Wool Dyes

As the preferred mordant, chromium salts soon became dominant and led to the development of a complete line of chromable wool dyes, all of which contain groups capable of forming metal chelates in the form of 5- or 6-membered rings. These dyes are still being sold in large quantities because of their excellent fastness properties, although the metallization treatment, which is carried out by the dyer, usually causes some dulling of the final shade. The first members of the group of chromable azo wool dyes contained the salicylic acid structure. This structure also is utilized in a high-quality triphenylmethane type wool dye which was introduced to the trade 50 years ago and is still quite important commercially. It is offered by all major manufacturers of organic dyes in the form of the reddish-orange colored disodium salt of the unmetallized color base. The trade name and structure of the current Du Pont brand are shown below; a postulated formula for the blue chromium complex will be discussed later:



Pontachrome Azure Blue BR, Mordant Blue 1 (C.I. 43830)

Pigment Lakes

Around 1900 the water- and oil-insoluble calcium, barium, and somewhat later the strontium salts or lakes of originally water-soluble azo dyes containing sulfonic or carboxylic acid groups in the molecule, became available to the industries consuming colored pigments. Today, the azo lakes, known as Lithols, are on a poundage basis the most important single group of organic pigments.

Premetallized Azo Dyes (1:1 Complexes)

Alfred Werner, author of the classical coordination theory (1893–5), published in 1908 a fundamental paper (*6*) on the theory of mordant dyes, and eight years earlier Bamberger (*7*) reported the isolation of an

"alcohol-insoluble copper salt" from *o,o'*-dihydroxyazobenzene (announced 37 years later by Pfeiffer and coworkers (*8*) as a new compound). However, the technology of metal complexes from this now important type structure remained stagnant for some time. In 1919 the Swiss firm Ciba, and the I. G. in Germany made a major advance in the use of cyclic metal chelates by introducing the pre-metallized (1:1 dye:metal) dyes represented by their Neolan and Palatine Fast brands, respectively. The use of these pre-chromed dyes avoids the troublesome metallization *in situ*, which, in dyeings with the unmetallized mordant dyes, must be carried out by the dyer as part of the dyeing process. According to the conventional (*A*) "pre-, (*B*) meta-, or (*C*) afterchrome" dyeing methods, (*A*) the wool is treated in the dye bath, prior to the addition of the unmetallized dye, with an excess of sodium dichromate, or (*B*) the sodium dichromate is added to the hot dye bath some time after the wool has been added, or (*C*) the exhaustively dyed wool is aftertreated in a separate bath with the metal salt to develop the final shade and desired fastness properties of the dyeing. Some pre-chromed 1:1 dye:metal complexes are still widely used as wool dyes, while specially designed pre-coppered *o,o'*-dihydroxy (and *o*-carboxy-*o'*-hydroxy) azo dyes are valued as direct cotton dyes. The first systematic investigation of this type of metal (chromium and cobalt) complexes was discussed in 1924 by Morgan and Main Smith (*9*). A more detailed study of 1:1 copper complexes from *o*-hydroxyazo structures was reported in 1938 by Drew and Lanquist (*10*), whose work supported an earlier study by Pfeiffer and his co-workers (*11*) on chelated dyes of this type. The name "chelate," from the Greek *chēlē*, claw, was first proposed in 1920 by Morgan and Drew (*12*) for "caliperlike groups which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings."

More recent studies of the copper complexes from *o,o'*-dihydroxy azo dyes containing sulfonic acid groups, were reported in 1940 by Beech and Drew (*13*). In 1952 Guido Schetty (*14*) presented his scholarly studies with chromium complexes of this type.

Neutral Dyeing 2:1 Complexes

The commercial success of the (1:1) types of premetallized wool dyes greatly stimulated academic and industrial research on metallized dyes. In 1939 Drew and Fairbairn (*15*) published the results of their systematic studies on the conventional 1:1, and also on newly discovered 2:1 types of dye:chromium complexes. The latter were obtained by reacting 1:1 chromium complexes from *o,o'*-dihydroxy (or *o*-hydroxy-*o'*-carboxy) azo dyes with a second molecule of the same or of a similar azo dye. The "acid chromicomplexes" which they obtained by this method from such azo dyes which were devoid of sulfonic or other acid groups, were found to be soluble in aqueous alkalies, ammonia, or organic bases. They were found to behave in aqueous alkaline solution as an anion with one negative charge carried by the entire dye-metal complex. Intense industrial process and product development work was carried out on these new neutral dyeing 2:1 complexes simultaneously, but independently by chemists of the German firm now organized as the BASF in Ludwigshafen (*16*) and by chemists of the Swiss firm, Geigy (*17*). The discovery that these neutral dyeing chromium and cobalt complexes, unlike the older 1:1 metallized wool dyes, are eminently useful for the dyeing of polyamide type fibers represented by DuPont's nylon and the German fiber Perlon, was first disclosed in the 1940 German Patent 734,990, with J. Müller and H. Pfitzner as the inventors. This was followed immediately by the commercial developments of the first German dyes of this type which were offered as Perlon Fast brands. Pfitzner is also one of the inventors in the 1941 German patents 743,155 and 745,334 which are claimed (*18*) to be the first disclosure of the use of the sulfamoyl substituent which imparts to these 2:1 complexes a favorable degree of solubility in the dyebath. The presence of this and of alkylsulfonyl groups also was shown to improve greatly the affinity of these complexes to wool, thus making it possible to dye this fiber with these modified 2:1 complexes in attractive shades of excellent fastness properties.

2:1 chromium and cobalt complexes made from both old and new azo dye structures are now produced by most major American and foreign manufacturers of organic dyes.

This latest phase of academic and industrial research on metallized textile dyes is still in full swing throughout the entire civilized world. Making use of the latest bonding theories and the most modern physical research tools, especially X-ray and infrared analyses, great contributions have been made toward elucidating the structures of metal complexes, by such outstanding American scholars as Melvin Calvin and Arthur E. Martell (*19*), John C. Bailar (*20*), Conard Fernelius (*21*), and by many others.

The pioneering research carried out by the English workers (*9*, *10*, *12*, *13*, *15*) in applying Werner's coordination theory to metal complexes of dyes, especially to those representing the *o,o'*-dihydroxy azo structure, has also contributed greatly to the commercial development of all types of metallized dyes. An informative discussion of the dyeing and other properties of the (1:1) chromed acid dyes for wool, and also of the dyeing of wool with commercial (2:1) metallized *o,o'*-dihydroxy azo dyes, was published in 1958 by J. F. Gaunt (*22*).

Other prominent European scientists, in addition to those already named, made major contributions in the form of up-to-date papers or reviews on metallized dyes; these include Zollinger (*23*, *24*) in Switzerland and Wittenberger (*25*) in Germany, where, in 1954, Pfitzner (*26*) also published an excellent review of the industrial research carried out by his firm toward the development of the commercially important types of 2:1 metallized azo dyes.

Phthalocyanine Pigments

The most spectacular achievement in the field of modern organic metallized pigments is the discovery and commercial development of the metal phthalocyanines, among which copper phthalocyanine and its exhaustively chlorinated derivative are of outstanding commercial importance. These extremely durable

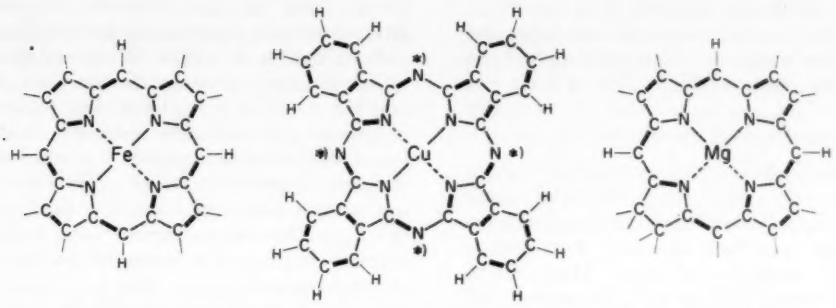
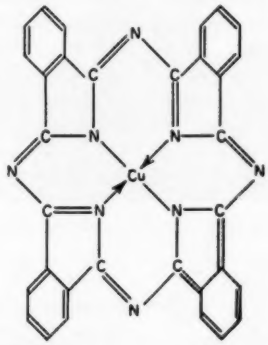


Figure 1. Structures of hemoglobin (left) and chlorophyll (right) compared with that of copper phthalocyanine. (After Mühlbauer (27).)

pigments, represented by DuPont's Monastral[2] Fast Blue and Fast Green brands, and the textile dyes and solvent-soluble derivatives, all of which contain the phthalocyanine structure, make use of the only really new chromophore discovered in the last 50 years. This is the planar 16-membered porphyrin ring with the metal in the center, represented by copper phthalocyanine which is the tetrabenzo-aza-porphyrin of the structure shown below.

It is intriguing to observe the striking structural similarity which this, the best of all presently known man-made pigments, has to the natural metal complexes represented by hemoglobin and chlorophyll, which are the iron and magnesium complexes, respectively, of porphyrin, and without which animal or plant life, as we know it, could not exist. An illustrative comparison of these three structures, as presented in an article written on this subject by Mühlbauer (*27*) in the magazine published by his firm (BASF) is reproduced above.

It is a fascinating story (*28*, *29*), how the first (1927) literature disclosure on the preparation of a blue compound (now known to have been copper phthalocyanine) by the Swiss chemists de Diesbach and von der Weid (*30*) did not arouse any interest because they suggested in their brief paper that their product was a



Copper phthalocyanine

[2] This is a registered trademark, originally used by Imperial Chemical Industries (England) for their commercial brands of phthalocyanine pigments. The name is now also used for some pigments of a different chemical type, which possess the durability and other characteristics associated in the trade with Monastral pigments.

pyridine complex of a "blue indigo," and why a group of alert chemists, employed by Scottish Dyes Ltd., deserve the main credit for this great discovery. Their diligent and persistent investigation of a blue impurity (now known to have been iron phthalocyanine) in technical phthalimide, and the complete elucidation (chemical formula and geometry) of the phthalocyanine structure by Professor R. T. Linstead and his coworkers, rank among the most brilliant and inspiring achievements of industrial and academic research. A good summary of the latter studies was published in 1936 (*31*).

Fundamental Properties of Metal Chelates

The most useful chelating groups, which must be located in a favorable position in the dye molecule in order to form cyclic chelates, are the —OH, —COOH, —N=, —NH—, and —NH_2 groups. The most important of these commercially are the —OH and —COOH groups located either ortho to each other, or in the peri (*1*, *8*) positions in a naphthalene structure, or ortho to the azo group (*32*). In order to achieve adequate thermal and hydrolytic stability of the chelate ring, the chelating groups must be so arranged geometrically that formation of the relatively stable 5- or 6-membered chelate rings is favored.

Not considering further the simple lake type pigments, in which the metal (usually Al, Ca, Ba, or Sr) is attached to the salt-forming groups by regular ionic bonds, and also discounting the special case of the cyclic iron(III) chelate present in the Naphthol Green made from 1-nitroso-2-naphthol, there are only three metals used to a significant extent in the commercial types of metallized dyes or pigments, namely copper(II), chromium(III), and cobalt. Except for the unique vat dye known as Indanthrene Brilliant Blue 4G, C. I. 74140, which represents partly sulfonated cobalt phthalocyanine, discovered in 1948 by chemists of the Bayer Company in Germany (*33*, *34*), the use of cobalt in commercial metallized dyes is at present restricted to the 2:1 metal complexes from *o,o'*-dihydroxy azo dyes.

Types of Bonds and Stability

For an understanding of the structure of the cyclic metal chelates and the bonds which hold the metal

more or less firmly in the dye molecule, it is important to realize that in this use the metals are characterized by their coordination numbers which are 4 for copper and 6 for chromium and cobalt. This defines the maximum number of donor groups which can normally become attached at one time to the selected metal atom.

When the bonding tendency of the central metal atom is fully satisfied, as is the case in copper phthalocyanine and in some other "inner" complexes, the metal chelates are extremely stable, and their solutions show practically no electrical conductivity (*35*). More often, however, especially when dealing with chromium and cobalt complexes of *o,o'*-dihydroxy azo dyes, the chelating groups in the dye molecule do not exhaust all of the metal's bonding forces. This enables the metal to form further bonds with other molecules such as water, ammonia, and organic nitrogen bases, and with active sites available in the fiber to be dyed (*36, 37*).

Each of the two azo nitrogens in metallized *o,o'*-dihydroxy azo dyes could be expected to form a bond with the chelating metal, but it is apparent that the azo group occupies only one of the coordination positions available in the sphere of the metal ion (*38*). Contrary to the practice adopted in some textbooks and other literature references, and for the reason indicated above, we favor illustrating this type of bond by an arrow reaching from the middle of the double bond between the two azo nitrogens to the symbol of the metal.

In general, any organic compound displaying intramolecular hydrogen bonding will react with metal ions to form a chelate ring. The driving force with which the *o,o'*-dihydroxy azo structure forms a cyclic chelate with the metal ions is so great that in place of the free hydroxy group, the corresponding *o*-methoxy or even the *o*-chloro azo dye may be used to produce the same final product, provided that sufficiently stringent metallization conditions are employed to cause demethylation of the methoxy group or hydrolysis of the chlorine in the ionizing solvent. The use of selected *o*-methoxy or *o*-chloroarylamines as the original diazo components avoids the difficulty arising from the low coupling energy of diazotized *o*-aminophenols, thus making it possible to synthesize metallized *o,o'*-dihydroxy azo dyes which otherwise are not readily available (*38*). In some cases the *o,o'*-dihydroxy azo metal chelates can also be obtained by subjecting the corresponding mono-*o*-hydroxy azo dyes to an oxidative coppering treatment (with aqueous copper sulfate, sodium acetate, and H_2O_2 or peroxides at 40–70°C and a *p*H of 4.5–7.0) according to a newly-published method (*39*). This 1958 paper by Pfitzner and Baumann also discloses the conversion of some of the coppered azo dyes thus obtained to the corresponding 1:1 and 2:1 chromium complexes by a metal exchange reaction. Under non-oxidative metallization conditions, the azo dyes which contain only one hydroxy in a position ortho to the azo group form copper (but not chromium) complexes which, however, are too unstable to be of commercial interest as textile dyes (*40, 41*).

The metal in the cyclic chelates of most chromed azo dyes is held firmly in the dye molecule. In some cases the metal complex survives heating the dye in dilute sulfuric acid under pressure (to split off sulfonic acid groups from the dye molecule), or reducing a nitro group to the amino group, or even boiling with aqueous sodium hydroxide (*42*). However, the choice of the metal greatly influences the stability of the chelate, and the metal in a relatively less stable complex can, in general, be replaced by a suitable treatment with the ion of another metal capable of producing an analogous complex of greater stability. The relative stability of the various metals in a series of analogous, metallized dyes can thus be estimated (*43*), and the following stability rankings are indicated for the *o,o'*-dihydroxy azo dye chelates:

$$\text{Cr(III) or Co(III)} > \text{Cu(II)} > \text{Ni(II)}$$

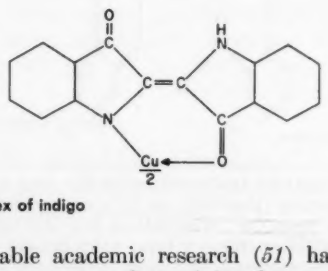
The metal complexes from *o*-carboxy-*o'*-hydroxy azo dyes behave similarly to those from the corresponding *o,o'*-dihydroxy structures (*44*). Those from the *o*-amino-*o'*-hydroxy azo structures are relatively less stable, but they also possess sufficient stability to be utilized in some commercial dyes. In other classes of dyes known to form metal complexes, the stability of the chelates varies greatly, depending on the choice of the metal, and on the type and location of the chelating groups involved (*45*).

In the planar copper phthalocyanine the formation of the fused, fully interlocked rings around the central metal is believed to be mainly responsible for the extreme stability of this metal complex structure, which can be sublimed in the absence of air-oxygen without decomposition at temperatures as high as 500°C, or sulfonated with oleum without suffering demetallization (*46*).

Among other factors which are known to influence the stability of specific metal chelates, the resonance effect in the chelate ring is of some significance (*47*). It is conceivable that in the chelates from the *o,o'*-dihydroxy azo structure (where either of the two azo nitrogens may be represented as engaged in the formation of the inner complex) this effect may be a factor contributing to the excellent stability of these favored metal complexes.

Geometrical Aspects of Chelate Structures

The influence of steric hindrance and of stereoisomerism on the formation and stability of cyclic metal chelates has been studied by many workers (*48*), but stereoisomers from commercial dye or pigment complexes are unknown. In 1922 Kunz (*49*) described a theoretically interesting, but relatively unstable copper complex of indigo for which Bailar (*50*) published the formula shown below, in which the trans form of indigo is represented as being selectively fixed by the chelating metal.



Copper complex of indigo

Considerable academic research (*51*) has been devoted in recent years to determining the exact geometric

arrangement of the metal chelate structure in typical pre-metallized dyes. It is generally accepted that covalent bonds are directed in space, while primarily ionic bonds are not. For covalent bonding the directional distribution of the donor groups will depend on the angular distribution of the metal orbitals which are available for bond formation. In the cyclic chelates used in dyes, in which the metal has the coordination numbers of either 4 or 6, the steric arrangements of the valences are tetrahedral, planar (square), and octahedral. Octahedral structures of Co(III) metal complexes have been studied more widely than any of the others, although the complexity of the problems involved has so far prevented the successful use of single crystal X-ray analysis, which is the only method capable of precise and complete determination of the structure of a complex or chelate. The highly successful use of this excellent tool of modern physics in determining the structure of planar tetradentate chelates, such as the cobalt chelate of *N,N'*-disalicylidene ethylenediamine, of an *o*-hydroxyacetophenone, and especially Robertson's Fourier analysis of the X-ray diffraction patterns of single crystals of phthalocyanine and its metal complexes (*52*), constitute the most spectacular advances in the last 25 years in the study of the theoretical aspects of metal complexes.

An illustration of the geometry and dimensions of the atoms in the copper phthalocyanine molecule, taken from the article by Mühlbauer (*27*), is shown here:

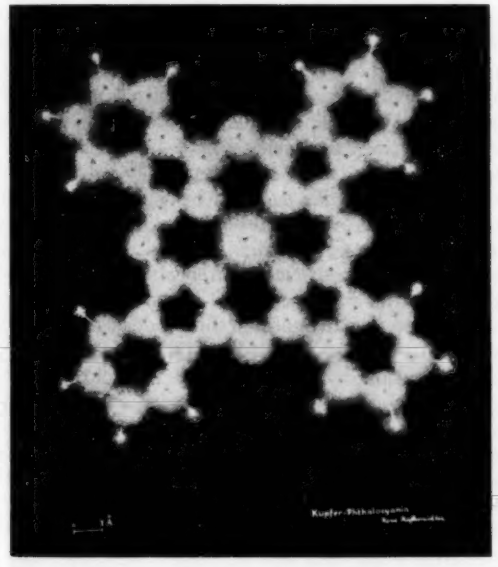
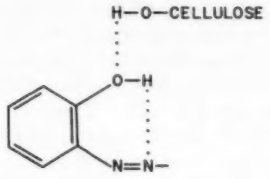


Figure 2. Geometry and dimensions of copper phthalocyanine. (After Mühlbauer (27).)

Dye-Metal-Fiber Interactions

Of much more direct interest to the industrial chemist are the chemical and physical interactions occurring between the dye, the metal, and the fiber. Bailar in his textbook (*20*) devoted several pages (763–67) to a well-documented discussion of these interactions.

In direct cotton dye complexes of the *o*-hydroxy (or *o*-amino) azo type, chelation can be expected to assist in the formation of hydrogen bonds between the dye molecules and the cellulose chain. For an unmetallized *o*-hydroxy azo dye the hydrogen bonding with cellulose may be illustrated as shown below:



Dye-cellulose hydrogen bonding

Bonding of the proton with the azo group is said to increase the accessibility of the electron pair involved in the formation of the hydrogen bond with the cellulose. It should be pointed out here that the significance of this hydrogen bonding is controversial. In very recent papers (*53*, *54*) strong support is offered for the conclusion that in normal dyeing processes, dye-cellulose hydrogen bonds are much less important than non-polar forces. As the decisive factor Zollinger (*54*) emphasized the geometry of the dye molecule, pointing out that a planar dye can approach the cellulose molecule so closely that strong van der Waals forces become the principal cause of attraction between the cellulose and dye. Since the copper chelate in metallized *o,o'*-dihydroxy azo dyes can be visualized as being planar, while the comparable chromium and cobalt complexes are undoubtedly non-planar structures, one may speculate that a difference in the geometry between these differently metallized dyes could explain the fact that only copper (not chromium or cobalt) complexes of selected pre-metallized (1:1) azo dyes exhibit sufficiently high affinity and fastness properties on the cellulosic fiber to be of commercial interest as direct cotton dyes.

Regenerated cellulose, such as viscose rayon, is equivalent in dyeing characteristics to the natural cellulose. The pre-metallized dyes cannot be used for the dyeing of cellulose acetate or of DuPont's Dacron polyester fiber. These fibers are devoid of reactive sites capable of bonding based on electron sharing. They are dyed commercially with "disperse" dyes, which involves an entirely different dyeing mechanism. In order to exhibit adequate affinity and fastness on these hydrophobic fibers, the dye molecule must be sufficiently small in size and of special design to permit its ready diffusion from the dyebath into the fiber by a solution mechanism.

In the dyeing of wool, as in the case of cotton, hydrogen bonding is believed to be a contributing factor, but the presence of basic as well as acidic groups in this fiber enables it to form other, relatively much stronger bonds with metallized acid dyes. Ender and Müller (*55*) and Valko (*56*) have studied in much detail the affinity of pre-chromed dyes for wool. As was summarized by Luttringhaus (*36*) and Wittenberger (*25*), wool is believed to form two different linkages with chromed dyes. As with the unmetallized azo dyes for wool, the presence of the sulfonic acid groups in the dye molecule enables it to form a salt linkage between the free dye acid and the wool. In addition to this ionic bonding, much evidence exists for the formation of a coordinate linkage between the metal in the chromium complex

and the basic groups of the wool. On the other hand, studies by Shuttleworth (*57*) have shown that the chief mechanism in the chrome tanning of leather with organic chromium complexes is coordination of the carboxy groups in the collagen protein with the chromium, while the amino groups do not coordinate appreciably. In applying the older type of chrome dyes for wool, dichromate ions (from sodium dichromate) are at first present in the dyebath. These ions are absorbed by the fiber where they are chemically reduced by the wool at the dyebath temperature to the chromium(III) ions needed for chelate formation.

Nylon can be dyed with chromable dyes, provided that the original dichromate is first reduced by the addition of a reducing agent to the dyebath, to produce the necessary chromium(III) ions (*58*), but commercially only the premetallized 2:1 azo dye:chromium or cobalt complexes, represented by DuPont's Capracyl brands, are used for the dyeing of nylon. According to present views (*24*, *59*, *77*), these complexes give nonmigrating and strong dyeings on nylon because a partial solution type dyeing mechanism is involved, based on the apparent fact that the 2:1 metal complex ion is hydrophobic and has very little solubility in water; it thus tends to pass from the aqueous dyebath into the fiber phase.

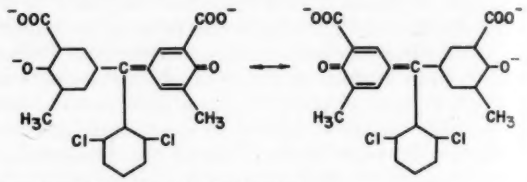
DuPont's Orlon polyacrylic fiber cannot be dyed with metallized dyes. For light and medium shades disperse dyes are useful, but to a much greater extent basic dyes are employed. On this fiber even some of the very old triphenylmethane dyes show surprisingly good fastness to light (*60*). Unmetallized acid dyes, preferably those of the anthraquinone class, were used commercially until a few years ago for the dyeing of polyacrylonitrile fiber by resorting to a special dyeing method which takes advantage of a unique type of fiber/metal/ion dye interaction. In this so-called "cuprous ion dyeing process" (*61*, *62*) the originally added copper(II) ions are reduced in the dyebath under carefully controlled conditions to copper(I) ions which attach themselves to the cyano groups. This permits discrete bonding with the larger acid or direct dye molecules which must contain one, but preferably not more than one, sulfo or carboxy group to be useful dyes for this fiber. The copper(I) ions are believed to form coordinate bonds with the —CN groups, and, upon addition of the dye, they form copper-dye linkages which may be schematically illustrated as shown below:

$$\text{Fiber}\cdot\text{C}\equiv\text{N}:\text{Cu}^{+}\ {}^{-}\text{O}_3\text{S}\cdot\text{Dye}$$

Much work remains to be done in the field of dye-metal-fiber interactions to gain a complete understanding of the chemical reactions which take place. The information concerning dye-metal interactions, while far from complete, is sufficiently advanced to enable reasonable predictions of the behavior of metal ions with numerous classes of dyes, but our knowledge of metal-fiber bonding is quite rudimentary, as is also our knowledge of the structure of the old, familiar metal chelate discussed below.

Salicylic Acid—Chelates

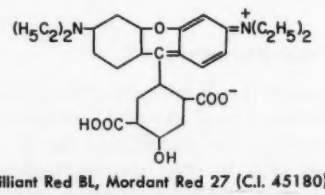
Strangely enough, the literature does not disclose a structural formula for this type of metal chelate (*25*), although advantage has been taken of its formation *in situ* for more than 50 years in the dyeing of some commercially important wool dyes. An outstanding example of these is the metallizable triphenylmethane dye which was mentioned earlier in this paper where the well-defined structure of the red-orange disodium salt of the color base, represented by DuPont's Pontachrome Azure Blue BR, was shown. The fact that the orange color of the unmetallized salicylic acid dye changes so drastically on metallization (with chromium, for example) to a strong and bright blue is specific for the triphenylmethane structure. By contrast, metal chelate formation involving the salicylic acid grouping in the azo dye molecule does not cause such a profound shade change. It is believed that in this triphenylmethane molecule a further, symmetrical, highly resonance-stabilized structure, represented below, may be responsible for this difference.



Pontachrome Azure Blue BR, blue complex

Commercial Aspects

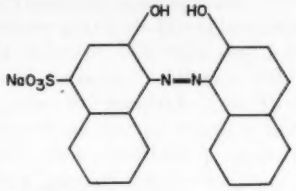
The marked increase in fastness properties, especially resistance to fading on exposure to light, and improved washing fastness, brought about by converting dyes with metallizable groups to their metal complexes, is for the user the most significant factor responsible for gaining for metallized dyes the dominant trade position they now enjoy. The relatively older types which were available prior to World War I in the form of unmetallized color bases, now are mostly used for dyeing wool in dark shades such as heavy maroons, navies, bottle greens, browns, and blacks where they show very good fastness to washing. They are comparatively dull and require a special, not readily controlled metallization treatment in the dye bath, but they are relatively less expensive than most of the modern pre-metallized dyes. Most of the newer chromable dyes are designed for application by the preferred metachrome dyeing process, and some of them give very attractive bright shades. An example of these is the dye shown in its unmetallized form below, which originally was offered in Germany just prior to World War II. Some of these chromable triphenylmethane type dyes also can be used for printing wool, cotton, cellulose acetate, and nylon, by employing a special printing method in which chromium acetate serves as the metallizing agent.



Chromoxane Brilliant Red BL, Mordant Red 27 (C.I. 45180)

The simple *o,o'*-dihydroxy azo dye which is marketed in its unmetallized form, represented by the formula shown next, ranks in respect to production rate among

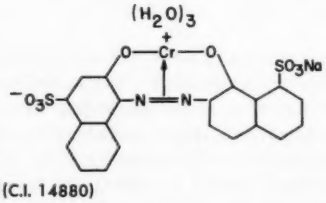
the highest of all chromable azo dyes made in the United States.



Mordant Black 17 (C.I. 15705)

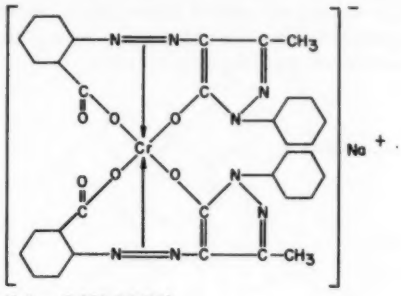
Also very important as a wool dye, and of special interest to the analytical chemist, is the similar *o,o'*-dihydroxy azo dye which has a nitro group in addition to the sulfo group in its diazo component and which is known as Eriochrome[3] Black T, Mordant Black 1 (C. I. 15710). This and related structures have become well known as metal indicators in colorimetric titrations, for instance in the determination of the hardness of water with the most widely employed metal complexing agent, ethylenediaminetetraacetic acid (EDTA). The latter method, and the use of this dye as a sensitive reagent in the colorimetric determination of trace amounts of magnesium and calcium, were first described in 1948 by Schwarzenbach and Biedermann (*63*). Conditions for using visual EDTA titrations, with Eriochrome Black T as the indicator, to determine many metal ions in water are summarized on page 619 of the December, 1959 issue (Vol. 36) of THIS JOURNAL. The determination of the metal in paint driers, taking advantage of this general method, was also described in 1959 (*64*).

As was mentioned earlier, the first pre-metallized azo dyes were marketed in Europe in 1919 as Neolan and Palatine Fast brands. Some 50 individual structures representing these (1:1) chromium complexes of *o,o'*-dihydroxy azo structures are commercially available, covering the entire range of shades. For their successful dyeing on wool, they require a strongly acid dyebath (*p*H *ca.* 1) which tends to damage the wool and to impair its highly valued softness to the touch. The dye illustrated by the formula shown below is one of the more important members of this group of pre-chromed dyes:

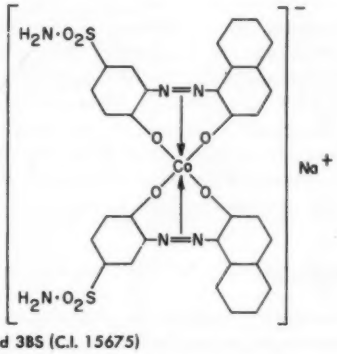


Acid Blue 158 (C.I. 14880)

Just prior to World War II the Germans began to offer a limited range of neutral-dyeing 2:1 complexes, in which the metal is either chromium(III) or cobalt(III), for the dyeing of Perlon and for use as solvent-soluble dyes; these were known as Perlon Fast or Zapon[4] Fast brands, respectively. A few of them, including two with cobalt as the metal, are included in the new edition of the Colour Index, where they are classified as (unnumbered) "Acid and Solvent Dyes." The structures for two typical Perlon Fast dyes are shown below in a favored presentation:



Perlon Fast Yellow G (C.I. 18690)



Perlon Fast Red 3BS (C.I. 15675)

The neutral-dyeing 2:1 complexes became available in America in 1949 where they found enthusiastic acceptance for producing pale and medium shades of high fastness, combined with surprisingly good migration properties. The fact that they are employed as sodium or ammonium salts and need only a trace of acid in the dyebath, renders them eminently useful for the dyeing of nylon. For the dyeing of wool they are preferably applied under moderate acidity (*p*H of 4–5) in the presence of an auxiliary agent with high affinity for the dye (*22*). These conditions do not impair the softness of the wool. Dyes of this type are widely used for the dyeing of wool, nylon, and "mixed" fabrics, including the newer kinds of carpets. They are simpler to apply than the older types of chrome dyes, and they undoubtedly will become more important as the requirements regarding fastness and brilliancy of shade become more stringent.

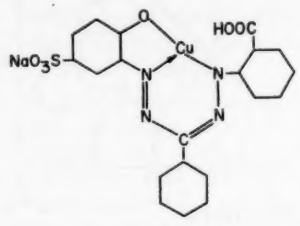
As the latest phase of this development, the major domestic and foreign manufacturers of textile dyes are actively designing unsymmetrical 2:1 dye:metal complexes, based on the previously mentioned discovery that the initial 1:1 complex can be combined, under certain experimental conditions, with a metallizable structure other than the original one. As an alternate, but much less readily controllable scheme, one may first make a molar mixture of two different *o,o'*-dihydroxy azo color bases and treat it with only one mole of the metallizing salt. In some cases the final mixture of dyes thus obtained, which might be expected to consist of a statistical mixture of the three theoretically possible symmetrical and unsymmetrical 2:1

[3] This is a trademark used for most of Geigy's (Switzerland) brands of chromable wool dyes.

[4] This German trade name was chosen to indicate that the dye thus named is specially finished to render it useful as a coloring component for I. G.'s Zapon (trademark for a synthetic resin) type lacquers.

metal complexes, shows surprisingly valuable tinctorial and application properties.

As an unusual type of metallized dye, the metal chelates from formazyl structures recently enjoyed renewed interest, although they were suggested 40 years ago for the dyeing of animal fibers (*65*). A representative member of this class of textile dyes is the blue-dyeing copper complex illustrated below:



Formazyl Blue

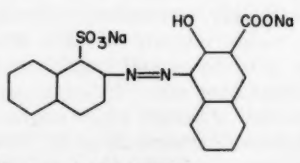
The unmetallized color base was shown by John H. Yoe and Rush (*66*) at the University of Virginia to be a highly sensitive reagent for the colorimetric determination of zinc ions in extremely dilute (1:50,000,000) solutions. The reagent is made by coupling diazotized 2-amino-1-phenol-4-sulfonic acid with the hydrazone prepared by reducing diazotized anthranilic acid to the hydrazine and condensing this hydrazine with benzaldehyde.

Metallized Pigments

The commercially important, man-made types of metallized organic pigments find their greatest use as the coloring component in printing inks and paints, for the coloring of rubber, for the dyeing of paper pulp from aqueous dispersion, and for the printing of textiles by the pigment printing method, in which the insoluble pigment is anchored to the fabric by heat-curable resins. This last-mentioned use of highly colored pigments was greatly stimulated by the advent of the copper phthalocyanine blue and green about 20 years ago. It is estimated that today approximately half of all printed goods, particularly ladies' dresses, are decorated by this inexpensive and simple printing method.

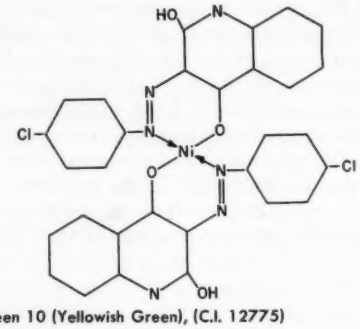
The formation of the alkaline earth or heavy metal salts of monosulfonated azo dyes offers the most direct method of imparting insolubility and useful pigment properties to a simple textile dye. The commercially important Lithol brands represent these lake-type pigments, which are made by coupling diazotized anilinesulfonic or carboxylic acids (anthranilic acid) to 2-naphthol or, preferably, to 3-hydroxy-2-naphthoic acid, followed by conversion to the calcium, barium, or strontium salts. In the Lithol Reds 2-amino-1-naphthalene sulfonic acid (named, after its discoverer, Tobias acid) is the preferred diazo component.

An interesting automotive maroon pigment is the manganese lake of the structure shown below for the disodium salt:



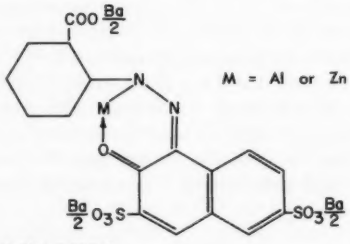
Pigment Red 63 (Bordeaux), (C.I. 15880)

Another unique automotive pigment is the nickel chelate of the structure shown below, which was discovered in 1946 in the Jackson Laboratory by taking advantage of the good metal-chelating properties of azo dyes in which 2,4-quinoline diol serves as the coupling component. This metallized product also is offered as one of DuPont's Lithosol brands, which are specially finished aqueous pastes, particularly suitable for pigment printing on textiles. This nickel complex shows unusual fastness to light, to heat, and to outdoor exposure.



Pigment Green 10 (Yellowish Green), (C.I. 12775)

The azo pigment made by coupling diazotized anthranilic acid to R acid (2-naphthol-3,6-disulfonic acid), followed by converting the dye to a cyclic metal chelate, is valued in the form of the barium salt, or lake, as a trichromatic red for high-class printing-ink work, particularly lithographing on tin. It is highly resistant to water and to oil, with outstanding stability to heat. This product probably has the structure indicated below (*67*):



Pigment Red 60 (C.I. 16105)

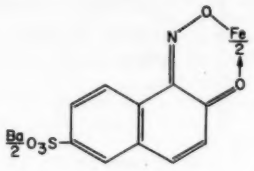
The aluminum lake of an old (1896) triphenylmethane dye derived from *N*-ethyl-*N*-benzylaniline, is still used in large quantities as a trichromatic blue in color prints, although it is fugitive to light and shows a water bleed that is objectionable in lithography (*67*). This product, Pigment Blue 24 (C. I. 42090), is widely known by Geigy's (Switzerland) original trade name, Erioglaucine A.

The aluminum complex from quinizarin-2-sulfonic acid (1,4-dihydroxy-2-anthraquinonesulfonic acid), known as Helio Fast[5] Rubine 4BL, Pigment Violet 5 (C. I. 58055), is a widely used pigment which is brilliant in shade, transparent, fast to influence of vehicles, and shows a high degree of fastness to light (*69*).

The first of the fully synthetic metal complex pigments, which was discovered in 1885 and still enjoys significant use, is the previously mentioned Naphthol

[5] This original German trade name was chosen to indicate its resistance to fading in sunlight (Greek *helio*—the sun).

Green. The barium lake, which is known as Naphthol Green B, Pigment Green 12 (C. I. 10020), has the structure indicated below:



Pigment Green B

Commercially more important is the unsulfonated form of this unique iron chelate. Discovered in 1921 by the BASF (*78*), this alkali- and soap-fast pigment, known as Pigment Green B and classified as Pigment Green 8 (C. I. 10006), finds considerable use in America in emulsion paints. Because of its fastness to most rubber cures, it is also valued as a rubber color (*79*).

Phthalocyanine Dyes and Precursors

In conclusion, attention is called once more to the outstanding metal phthalocyanine structure. It was natural that many, more or less successful, attempts were made to utilize this unique chromophore for the dyeing of textiles (*70*). The first dye of this type was the di(or tri)-sulfonated copper phthalocyanine, Direct Blue 86 (C. I. 74180), which serves as a cotton and paper dye. Its conversion to aliphatic amine salts produces dyes which are used in lacquers or spirit printing inks. One of the latter type is DuPont's Luxol[6] Fast Blue MBS which is valued as the coloring component in high-quality inks for ball-point pens, and which recently was found to serve as a selective stain for the combined staining of cells and fibers in the nervous system (*71*).

The unique use of one of the metal phthalocyanines as a vat dye is based on the discovery by German chemists (*33*) that partly (approximately 25%) sulfonated cobalt phthalocyanine, represented by Indanthrene Brilliant Blue 4G, Vat Blue 29 (C. I. 74140), can be reduced, like an anthraquinone vat dye, with dilute caustic and hydrosulfite to an ionized hydro compound which possesses moderate affinity to cotton and is capable of being oxidized *in situ* to the parent dye (*34*).

Outstanding also is the discovery (in 1944) by Haddock and Wood of the Imperial Chemical Industries, Ltd., that the introduction of four specially designed onium groups (which split off during the dyeing) into the copper phthalocyanine molecule gives a water-soluble direct dye which is represented by I.C.I.'s Alcian Blue 8GS, C. I. 74240. Haddock (*72*) also discovered that the introduction of several mercapto groups (or groups which during the dyeing are converted to mercapto groups) into copper phthalocyanine produces a green sulfur dye of the type represented by I.C.I.'s Thionol Ultra Green B and DuPont's Sulfogene Brilliant Green J (*73*).

The most ingenious method discovered to date for fixing copper phthalocyanine on the fiber is to synthesize a solvent-soluble precursor of the type represented by the structure shown below, which on reductive treatment *in situ* (usually carried out with dilute caustic and sodium hydrosulfite) is converted quantitatively to the beautifully bright greenish blue shades of copper phthalocyanine.

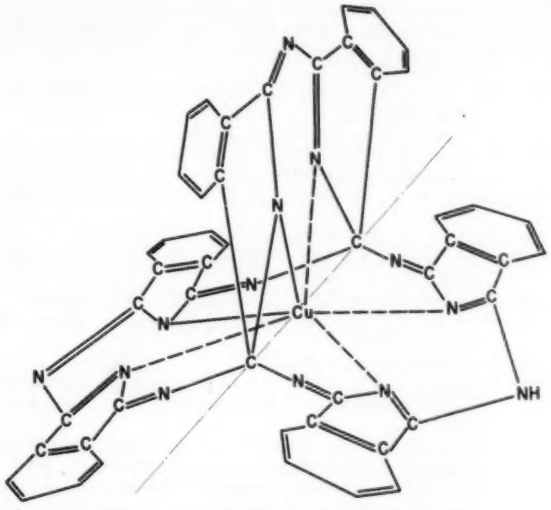


Figure 3. Structure of copper phthalocyanine precursor.

This three-dimensional structure requires the unusual coordination number six for copper. This illustration of the precursor is supported by the geometric arrangement of the atoms in a molecular model, and by considering its known physical and chemical properties. An effect of chelation in changing the usual coordination number of copper to six was observed in 1949 for a diethylenetriamine complex (*80*).

The synthesis and characterization of the above structure are contributions made in the Jackson Laboratory (*74*). Similar in principle and goal was the research which was carried out at a somewhat earlier date in Germany by chemists of the Farbenfabriken Bayer (*75*), and which led to the commercial development of related products, the most important of which is a metal-free precursor known as Phthalogen Brilliant Blue IF3G. The chemical characterization, and the use of all these phthalocyanine derivatives or precursors for textile printing are discussed in the reference (*73*) cited above.

As the latest German contribution to the use of the phthalocyanine structure for the dyeing and printing of textiles, the Bayer research laboratory developed a new azoic coupling component which is associated with the trade name Naphthol AS-FGGR (*76*). This phthalocyanine derivative is said to be particularly useful in combinations with conventional azoic diazo components for the dyeing and printing of various fabrics where it gives strong green shades of outstanding fastness properties. While this development is undoubtedly an important advance in principle and in technology, its commercial significance remains to be demonstrated.

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[6] This is DuPont's registered trademark for solvent-soluble diarylguanidine salts of dyes containing sulfonic or carboxylic acid groups.

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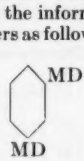
Chem Gems

Chem-gem-ology has achieved the stature of a branch of knowledge. At least it is possible to do literature research in the field. Professor A. L. Myers of Carson-Newman College, Jefferson City, Tennessee, builds on the information available in this Journal, **33**, 511 (1956) and **34**, 140 (1957) to define philosophers as follows:



(Metaphysicians)

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A Complete Table of Electronegativities

Although the concept of electronegativity is widely used for the correlation of various properties, there is as yet no complete table of electronegativity values available. The advantages of such a table for teaching purposes are numerous. For this reason this paper presents a complete table of such values based upon a single method of estimating this property. When the data required by the various methods are considered, it is readily seen that the best that can be done in this regard is to present *reasonable* estimates based upon a consistent procedure for all the elements. Subsequently, as more precise information becomes available, such a compilation can be revised to give more significant electronegativity values.

$$D(A-B) = \{D(A-A)\cdot D(B-B)\}^{1/2} + 23.06(X_A - X_B)^2$$

where

$D(A-B)$ = dissociation energy of $A-B$ in kcal/mole
$D(A-A)$ = dissociation energy of $A-A$ in kcal/mole
$D(B-B)$ = dissociation energy of $B-B$ in kcal/mole
X_A = electronegativity of A
X_B = electronegativity of B

or

$$Q = 23.06\,\Sigma(X_A - X_B)^2 - 55.1N_N = 24.2N_O$$

where

Q = heat of formation of the compound in kcal/mole
N_N = number of nitrogen atoms in the compound
N_O = number of oxygen atoms in the compound

Table 1. A Complete Set of Electronegativity Values

H																	He
2.1																	—
Li	Be											B	C	N	O	F	Ne
0.97	1.47											2.01	2.50	3.07	3.50	4.10	—
Na	Mg											Al	Si	P	S	Cl	A
1.01	1.23											1.47	1.74	2.06	2.44	2.83	—
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.91	1.04	1.20	1.32	1.45	1.56	1.60	1.64	1.70	1.75	1.75	1.66	1.82	2.02	2.20	2.48	2.74	—
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.89	0.99	1.11	**1.22**	**1.23**	**1.30**	**1.36**	**1.42**	**1.45**	**1.35**	1.42	1.46	1.49	1.72	1.82	2.01	2.21	—
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.86	0.97		**1.23**	**1.33**	**1.40**	**1.46**	**1.52**	**1.55**	**1.44**	**1.42**	**1.44**	**1.44**	**1.55**	**1.67**	**1.76**	**1.90**	—
Fr	Ra	**															
0.86	**0.97**																

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	1.08	**1.08**	**1.07**	**1.07**	**1.07**	**1.07**	**1.01**	**1.11**	**1.10**	**1.10**	**1.10**	**1.11**	**1.11**	**1.06**	**1.14**
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No?	
	1.00	**1.11**	**1.14**	**1.22**	**1.22**	**1.22**	**(1.2)**	**(1.2)**	**(1.2)**	**(1.2)**	**(1.2)**	**(1.2)**	**(1.2)**	**(1.2)**	

Value for hydrogen from Pauling (*1*).
Values in **bold type** are from this work.
Values in parentheses ( ) are rough estimates.
All other values are from Allred and Rochow (*10*).

There are at present, a large number of electronegativity scales but that of Pauling (*1*) has been almost universally accepted as a standard for comparison. The chief limitation on the extension of Pauling's scale to all the elements is the lack of suitable data. Pauling has given two alternative ways to calculate the electronegativities on his scale. These are summarized in the equations and the summation extends over all the bonds in the compound. The second equation is only an approximation and is not completely consistent with the first one, as it would require all compounds between elements of identical electronegativity (which do not contain nitrogen or oxygen) to have a zero heat of formation. So far it has been impossible to extend these equations or refined versions of them to all the elements. Where the required thermochemical data are available such calcula-

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tions have been made (*2–5*), but in some cases these extensions have led to values which are inconsistent with the original definition (i.e., with extensions of the second equation).

Another electronegativity scale which has a great deal to recommend it is one due to Mulliken (*6, 7*). This measures the electronegativity of a species A as $^1/_2(I_A+E_A)$, where I_A is the ionization potential of A and E_A is the electron affinity of A. This is related to the electronegativities on Pauling's scale by

$$^1/_2(I_A + E_A) - {}^1/_2(I_B - E_B) = 2.78(X_A - X_B)$$

The chief reason why the Mulliken scale is not used here is that it is not possible, at present, to get reliable estimates for the electron affinities of all the elements. The customary assumption that $E=0$ for most of the metals seems unwarranted. Thus the electron affinity of lithium has been estimated to be 0.81 ev (*8*). Using this figure and the ionization potential for lithium, X_{Li}-1.10; on the assumption that the electron affinity of lithium is zero, $X_{Li}=0.97$. While methods of estimating the electron affinity are available (*9*), these cannot yet be used with all the elements.

Of the remaining methods of calculating electronegativities, that of Allred and Rochow (*10*) is recommended by (*a*) the fact that it uses data which are either readily available or easily estimated and (*b*) its rather direct relation to the electronegativity scale of Pauling. It considers the electronegativity to be the force of attraction between the atom and an electron separated from the nucleus by the covalent radius. The screening of the intervening electrons is taken into consideration using Slater's rules (*11, 12*). This force is calculated using simple electrostatics, viz:

$$\text{Force} = \frac{e^2 Z_{\text{eff}}}{r^2}$$

These authors also established that the force calculated in this manner is related to the electronegativity on the Pauling scale in a simple fashion. The electronegativity on the Pauling scale is given by:

$$X = 0.359\,\frac{Z_{\text{eff}}}{r^2} + 0.744$$

A complete set of electronegativity values, calculated using this equation is presented in Table 1. Data on electronic configurations and covalent radii were obtained from standard references where possible (*13–16*). The radii used were, for the most part, taken from Pauling (*16*). The effective nuclear charge was calculated for the next s or p electron added to the atom. In some cases the covalent radii were estimated from those of neighboring atoms in the periodic table (e.g., Fr, Ra, Pm and Po). The value for actinium used is that given by Katz and Seaborg (*17*).

The values are given on the Pauling scale as this is the one which has been most widely used for correlations (*18, 19*). An alternative procedure which could be used to obtain a related set of numbers is that of Sanderson (*20*). Sanderson's scale is, however, less familiar to most chemists and has been used less widely for correlations. Another approach to the problem of the degree of polarity of chemical bonds has been given by Lakatos (*21*). Lakatos uses ideas very similar to those of Allred and Rochow but has developed them in greater detail in regard to the determination of the percentage of ionic character in bonds.

Table 2. Effective Nuclear Charges and Atomic Radii Used

Element	Z_{eff}	r(Å)	Element	Z_{eff}	r(Å)
Zr	2.80	1.454	Hf	2.65	1.557
Nb	2.45	1.342	Ta	2.95	1.343
Mo	2.60	1.291	W	3.10	1.299
Tc	2.75	1.267	Re	3.25	1.278
Ru	2.90	1.241	Os	3.40	1.255
Rh	3.05	1.247	Ir	3.55	1.260
Pd	2.70	1.278	Pt	3.20	1.290
Ce	2.50	1.647	Au	3.35	1.336
Pr	2.50	1.648	Hg	4.00	1.440
Nd	2.50	1.642	Tl	4.65	1.549
Pm	2.50	1.65	Pb	5.30	1.538
Sm	2.50	1.66	Bi	5.95	1.52
Eu	2.50	1.85	Po	6.60	1.53
Gd	2.65	1.614	At	7.25	1.50
Tb	2.50	1.592	Fr	1.85	2.40
Dy	2.50	1.589	Ra	2.50	2.00
Ho	2.50	1.580	Ac	2.65	1.88
Er	2.50	1.567	Th	2.80	1.652
Tm	2.50	1.562	Pa	2.65	1.55
Yb	2.50	1.699	U	2.65	1.42
Lu	2.65	1.557	Np	2.65	1.42
..	...	...	Pu	2.65	1.42

Improved or alternative values on this same electronegativity scale (Pauling's) can also be obtained using several other types of information. Some of these relations are:

Liu (*22*):

$$X = 0.313\left(\frac{n + 2.6}{r^{2/3}}\right)$$

where

n = number of valence electrons
r = covalent radius

Gordy (*23*):

$$X = 0.31\left(\frac{n + 1}{r}\right) + 0.50$$

where the symbols have the same meaning as in Liu's equation.

Gordy (*24*):

$$k = aN\left(\frac{X_A X_B}{d^2}\right)^{3/4} + b$$

where

k = force constant of bond between A and B
d = internuclear distance
a and b are constants

For the most part the electronegativity values calculated with these equations are rather close to those given by Pauling.

A perplexing question which arises in the construction of a complete table of electronegativities is that of obtaining suitable values of the inert gases. While it might be possible to extract numbers (real or complex) from data on spectroscopically observable species, it is more reasonable to go back to the original meaning of the term electronegativity: "the power of an atom *in a molecule* to attract electrons to itself" (*1*). Since the inert gases form no stable molecules it is best to leave these spaces blank. On first thought, a value of zero might seem appropriate. Such a choice would lead to considerable ambiguity in the use of the usual equations

Table 3. Sample Calculation (for Tungsten, Atomic Number 74)

Electronic configuration $1s^2 \ldots 5s^2\ 5p^6\ 5d^4\ 6s^2$

Z_{eff} = (atomic number) − (screening factor)
= 74 − (0.85)(No. of n = 5 electrons) − (0.35)(No. of n = 6 electrons) − (1.00)(No. of electrons with n = 4 or less)
= 74 − (0.85)(12) − (0.35)(2) − (1.00)(60) = 3.10

$$X = \frac{(0.359)Z_{eff}}{r^2} + 0.744 = \frac{(0.359)(3.10)}{(1.299)^2} + 0.744$$

X = 1.40

for defining numerical values. For these reasons no values have been assigned to the inert gases.

While the present table is satisfactory for instructional purposes, it is not proposed as an ultimate source of information on the electronegativities of the elements. Any reader who is interested in the fine points of such electronegativity assignments is advised to read the excellent summary of Pritchard and Skinner (*18*).

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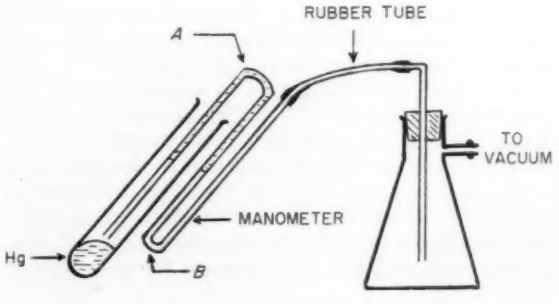
A Rapid Method for Loading Mercury Manometers

Frequently in the course of laboratory instruction in general chemistry it is necessary to fill a large number of mercury manometers. They can be safely and rapidly filled using the device illustrated below.

A 250-ml side-arm flask is stoppered and a glass tube is led about halfway down the inside of the flask. The side arm is then connected to a water pump and the manometer to the flask using rubber tubing. Mercury is placed in a 6-in. test tube or other vessel. The end of the inclined manometer is immersed in the mercury which is then permitted to advance up the tube to point *A*. Any deviation from this will give a longer or shorter column; trial and error can determine the best point to withdraw the manometer. When the column reaches point *B*, the vacuum is removed either by compressing the tube or better by slipping the tube off of the manometer using the thumb. However, this will require some practice.

The side-arm flask should be placed on a lower level than the working area so that any mercury drawn into the rubber tubing will flow immediately into the flask.



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Near Infrared Spectra

A neglected field of spectral study

The infrared part of the spectrum extends from about 2.0 to 25 μ (5000–400 cm^{-1}). Measurements in this region are commonly used to identify characteristic groups in a compound (*1*) or to analyze simple mixtures. However, very few studies have been made in the near infrared region which extends from about 2 μ into the visible at about 0.7 μ (20,000 Å to 7000 Å or 5000 to 1500 cm^{-1}) (*2*). Historically, near infrared radiation was detected before normal infrared radiation when Hershel, in 1800, observed that the spectrum of sunlight contained a component just beyond the visible red which could blacken a photographic plate or increase the temperature of a thermometer. The term "near infrared" formerly was used to denote the infrared spectrum to 23 μ (*3*) and to distinguish this region from that of the far infrared above 23 μ.

Problems in Instrumentation

The principal reason for the delay in the general study of near infrared spectra is that there has been no easy means of observing this part of the spectra until recently. On the other hand thermal-sensitive devices of relatively simple construction, such as the thermocouple and the bolometer, discovered by Julius in 1892, are sensitive to normal infrared radiation, and their use has led to a steady development in true infrared spectroscopy (*4*). These receivers, however, are not sensitive to near infrared radiation and early workers used photographic plates sensitized to the red part of the spectrum. However the spectra so obtained consist of a series of lighter and darker lines on the negative plate (corresponding to minima and maxima of the spectra), and the relative intensities of these lines must be measured with a photodensiometer (*5*). The use of this technique has led to the term "photographic" infrared to indicate the near infrared region (*6*).

Special methods have sometimes been used to record near infrared spectra, such as receiving the radiation on a phosphor and measuring the radiation of shorter wavelength emitted by the phosphor with a photomultiplier tube. However for the automatic recording of near infrared spectra some type of photoelectric cell must be used, and this has led to a further name, the "photoelectric" infrared (*7*). The photoemissive type of photoelectric cell, such as the cesium cell, in which the incident light causes the emission of electrons from a photocathode, can be used to about 1.3 μ and a photovoltic cell, such as the selenium layer cell, in which light produces a voltage difference across the cell, can be used to about 0.8 μ (*5*). However the only type of photoelectric cell which is operative throughout the near infrared region is the photo-conductive type, in which the conduction of an inorganic salt changes with the intensity of incident light (*4, 7*). The photoconductive effect (*8*) was not discovered until 1917 when Case observed that certain minerals such as galena (PbS), stibnite (Sb_2S_3), and bismuthinite (Bi_2S_3) have an increased conductance in the presence of light. However it is only within the last few years that photoconductive detectors have become commercially available. These are usually of synthetic lead sulfide which is sensitive to 3 μ. Lead telluride and lead selenide cells are sensitive to 4.0 and 5.4 μ, respectively, and the effective range of photoconductive cells is increased considerably by cooling them to a low temperature. Recently it has been reported that an indium sulfide cell is sensitive to 10 μ, and in the future photoconductive cells sensitive throughout the infrared region probably will be available.

The source of near infrared radiation is usually the tungsten lamp ordinarily used in visible spectrometers, and these lamps give continuous radiation up to 3 μ although they cannot be used above this since the glass envelope absorbs radiation of higher wavelength. An ordinary incandescent lamp can also be used up to 2 μ (*5*).

The optical material for prism spectrometers also presents no problem since good quality natural or synthetic quartz transmits light to about 3.0 μ (*7*), and, moreover, its maximum dispersion occurs at 2.9 μ. Optical flint glass is of limited use since it transmits to only 1.5 μ. The crystals used in infrared spectrometers, such as sodium chloride, lithium fluoride, and fluorite (natural calcium fluoride), also transmit near infrared radiation, but these materials are more expensive and less convenient than quartz.

The instrumentation of automatic recorders for the near infrared is well worked out (*9*), and commercial instruments are now available which measure to 2.8 or 3.3 μ (the Beckman D.K. 1 and 2 models, the Carey model 14, and the Perkin-Elmer Spectracord model 4000). The conventional Beckman D.U. instrument can be used effectively to 1.4 μ and can be modified to read to 2.7 μ by using a lead sulfide receiver in conjunction with a light modulator and recorder.

Origin of Near Infrared Spectra

Absorption in the infrared part of the spectrum arises from quantized energy changes in the frequencies of vibration and rotation of covalent bonds. The fundamental stretching vibrations of simple bonds (S in the diagram) are associated with maxima in the region 2

to 10 μ (except for bonds with heavy halogen atoms) and the "rocking" (R in diagram) or bending vibrations give rise to maxima from 10 to about 20 μ. If these

vibrations behaved as simple harmonic vibrations no other bands should be observed, but a number of much weaker bands are always encountered below 2 μ. These arise from the fact that the vibrations in bonds are not completely harmonic, and the equation, derived from quantum mechanical considerations (*10*), relating the various observed frequencies is

$$\nu = \{1 - (v + 1)x\}v.\omega$$

where ω is the natural frequency of vibration of the bond, v is a vibrational quantum number and can have values $v = 1, 2, 3$ etc., and x is the anharmonicity constant to correct for the anharmonic nature of the vibration. The frequencies of the various maxima (ν_1, ν_2, ν_3, etc.) will thus be

$$\nu_1 = (1-2x)\omega;\ \nu_2 = (1-3x)2\omega;\ \nu_3 = (1-4x)3\omega$$

for values of $v = 1, 2, 3$. The first frequency (ν_1) is termed the fundamental or first harmonic and the second frequency (ν_2) is the first overtone or second harmonic, etc. The value of x is very small, being between 0.01 and 0.05 for carbon-hydrogen vibrations, and the various overtones appear at nearly double, triple, etc. of the fundamental frequency or one half, one third, etc. of its wavelength (λ) (λ(in cm) = $1/\nu$ (in wave numbers)).

Apart from the overtone bands the frequencies of vibration of two or more bonds can combine together to produce a combination band, having a frequency which is the sum of the other frequencies. The form of a near infrared spectra with overtones and combination bands is very similar to that of the ordinary infrared.

Characteristic Bands

The fundamental stretching vibrations of bonds between relatively heavy atoms such as carbon, oxygen, and nitrogen give rise to maxima from 6 μ to 10 μ and the maxima of bending vibrations are above 10 μ. Consequently the first overtones of these vibrations will occur above 3 μ and will be submerged in the fundamental maxima of the vibrations of bonds containing hydrogen, such as carbon-hydrogen, oxygen-hydrogen, and nitrogen-hydrogen bonds. These groups have their fundamentals near 3 μ and their overtones will be observable in the near infrared below 2 μ (see Table I).

Table I.

Group	Wavelengths (in microns) Fundamental	Overtones	
C—H	3.5	1st	1.8
		2nd	1.2
		3rd	0.85
		4th	0.7
O—H, N—H	2.8	1st	1.4
		2nd	0.95
		3rd	0.7

The intensities of the various overtones, however, vary considerably (the molar absorbancy coefficients of the first and second overtones of carbon-hydrogen bonds being about 0.6 and 0.1, respectively), and only the first few overtones will be readily observable.

The most commonly used solvent is carbon tetrachloride since its carbon-chlorine bonds have their fundamental at 12.55 μ and the compound has only low absorption in the near infrared. However ethanol and benzene and other hydrogen-containing solvents can be used if their overtones do not obscure the overtones being studied in the solute.

The first infrared spectra of organic compounds were actually determined photographically from 0.7 to 1.2 μ by Abney and Festing in 1881, who made the very astute observation that "the foundation of all absorption in these bodies is the hydrogen." Coblentz between 1900 and 1920 did much pioneer work on the near infrared spectra of organic compounds while working at the Carnegie Institute in Washington and later at the National Bureau of Standards. The first high resolution near infrared studies were made by Brackett in 1928, who observed that primary (CH_3), secondary (CH_2), and tertiary (CH) hydrogen atoms attached to carbon gave bands at slightly different wavelength near 1.2 μ (the second overtone). Some confusion exists in the early literature concerning the numbering of carbon-hydrogen overtones since it was believed that the band at 6.9 μ in organic compounds was the carbon-hydrogen fundamental (although it is now known to be the carbon-carbon stretching fundamental), and the carbon hydrogen stretching fundamental at 3.5 μ was assumed to be the first overtone of the 6.9 μ band.

The differences noted by Brackett have since been observed in all the first four carbon-hydrogen overtones and recently bands at 1.63, 1.62, and 1.65 μ have been assigned to carbon-hydrogen bonds on double bonds (H—C=C—), terminal methylene groups (C=CH_2), and terminal epoxy groups (—C—CH_2) respectively,

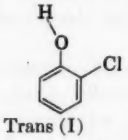
although these must be combination bands.

Hydrogen-Bonding

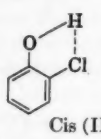
Perhaps the greatest use of near infrared spectra has been in the study of hydrogen bonding both intermolecular (between two different molecules) and intramolecular (within the same molecule). The amount of intermolecular bonding varies with the concentration, and the relative intensities of the two maxima near 0.95 μ given by free and bonded hydroxyl groups has been used to determine the amount of association. In alcohols such as methanol and isobutanol the molecules exist as groups of three or four. At higher temperatures the extent of hydrogen bonding is reduced and in the case of phenol the oxygen-hydrogen overtones, but not the carbon-hydrogen overtones change in wavelength. Recently it has been shown that β-phenylethanol ($C_6H_5CH_2CH_2OH$) has a doublet near 1.42 μ which is not present in the higher or lower homologues, 3-phenyl-1-propanol ($C_6H_5CH_2CH_2CH_2OH$) and benzyl alcohol ($C_6H_5CH_2OH$). This extra bond was attributed to hydrogen bonding between the hydroxyl group and the π-electrons above the first carbon atom in the aromatic ring.

Phenol- and para-substituted phenols have a single maximum at 1.42 μ in carbon tetrachloride solution.

However *o*-halogenophenols show a second peak near 1.45 μ even in very dilute solution. Pauling was the first to suggest that the extra maximum was due to internal (intramolecular) hydrogen-bonding. An *o*-halogenophenol, such as *o*-chlorophenol, can exist in two forms; the *s*-trans form (structure I) in which the hydroxyl hydrogen atom is opposite to the chlorine



Trans (I)



Cis (II)

atom, and the *s*-cis form (structure II) in which these atoms are brought close to each other, being *cis* with respect to the carbon-oxygen single bond. In this form (II) hydrogen bonding is readily possible, but the amount of the *cis* form decreases with increasing temperature, since the hydrogen bonds are thermally unstable. By measuring the relative changes in intensity with temperature of the two bonds it is found that the stabilizing energy ($\Delta\Delta F$) of the *cis* form is 1.4 kcal mole^{-1}.

Analytical Applications

The differences in the wavelengths of overtones of carbon-hydrogen bonds in different environments can be used to determine the relative proportions of saturated and unsaturated rings present in hydrocarbons as well as to determine the percentage of aromatics or olefins in mixtures (*11*).

Variously substituted hydroxyl groups also give distinct maxima which can be used to analyze water in hydrocarbons or in alcohols, acids in hydrocarbons or in anhydrides, and alcohols in hydrocarbons or in acids. In the same way the amine content of hydrocarbons can be obtained. All these measurements are sensitive to at least 0.1% (*11*).

It follows from this summary of near infrared spectra that this region is of considerable theoretical interest as well as having wide analytical application and is a part of the spectrum which merits more attention.

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Division of CHEMICAL EDUCATION

American Chemical Society

Nominations for Officers, 1960–61

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Karol J. Mysels, Professor, University of Southern California, Lic-es-Sc., Lyon (France); Ph.D., Harvard. Colloid and surface chemistry are the focus of his interests. He is recognized not only as an author of papers and books in his speciality, but also as coauthor of a textbook in general chemistry. Readers of this Journal benefit from his initiative and discernment as the chemical sleuth who uncovers and solves educational crimes as reported in the popular Textbook Errors Series.

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Martensite Transformations and the Phase Rule

Martensite reactions constitute an interesting and unusual class of phase transformations. They occur only as solid-solid reactions, and their behavior, which generally also serves as a definition of the term, will be described later. Martensite reactions are not widely understood beyond the realm of metallurgy, and they are not easily reconciled with the phase rule. It appears likely that the martensitic character of many phase changes in other than metallic systems has gone unrecognized. The purpose of this paper is to draw attention to their existence and their properties, in the hope that such a discussion will lead to the identification of many more martensitic phase changes in inorganic systems. Without entering into the controversies that still becloud the detailed analyses of many martensite transformations, brief mention will be made of the theories that lead to an understanding at least of their salient features.

Many martensite transformations constitute metastable equilibria. This, however, is not one of their essential characteristics, since some are equilibria between stable phases. The phase rule does not distinguish between stable and metastable equilibria; it applies equally and indifferently to both (*1*). Whether this is mainly a matter of practical experience or is to be expected on theoretical grounds, as this author believes, is the subject of opposing views with which we do not wish to be involved here. The concept of metastability has at times been applied rather loosely. It is used here in its strict application, where a metastable equilibrium is a true, reversible state of equilibrium between the phases involved, with $\Delta F = 0$, approachable from either direction at least over a limited range of the variables. It differs from the stable or "ultimate" equilibrium only in that the phases involved in the metastable equilibrium are not the most stable ones known to be possible in the system.

All recorded martensite transformations, except those in plain carbon and relatively low alloy steel, have been shown to be reversible (*2*). In the exceptions, the speed of decomposition to other phases is high. With this reservation then, it would be gratifying to find that martensite transformations, those producing stable and metastable phases alike, are not in contradiction to the phase rule.

The phase rule is a thermodynamic law and as such is indifferent to the atomistic nature of matter. Surface forces arising as they do from the subdivision of matter, are among those assumed to be negligible in the application of many thermodynamic laws. Consequently, caution is necessary when one treats extensively subdivided systems where the surface forces may be appreciable. In crystalline systems, there is in addition the possibility of having a considerable amount of strain energy. A phase change is thought to assume martensite character when this possibility is realized and the strain energy becomes large enough to influence the observable behavior of the system.

Some of the phase changes that occur in the solid state are initiated by the tilting or shearing of rows or planes of atoms, perhaps starting at dislocations, rather than the migration (diffusion) of individual atoms. In such a case, it is often true not only that the new phase possesses a surface area that is large compared to its volume, but also that the lattice strain energy is high. The presence of these nonnegligible strain and surface energies may be the reason why such phase transformations exhibit properties which differ from those of classical phase changes, and which cause them to be classified as martensitic. The specific properties of martensite transformations will now be reviewed, and then reference will be made to theories in which these properties have been explained by an application of the above ideas.

Occurrence of Martensite Transformations

Historically, the first martensite reaction to be recognized as having such unusual characteristics was the austenite-to-martensite transformation in steel. Because of its great practical importance, metallurgists were alerted early to the existence of this type of phase change and have since discovered many other examples in alloys and, more recently, in pure metals as well.

Examples of alloy systems in which martensite transformations occur are many varieties of steel, Cu alloys with Sn, Zn, and Al, the Fe-Ni, Fe-Mn, and Fe-Co-W systems. References concerning these systems have been collected by Troiano and Greninger in their review article (*2*). Other interesting cases have been found in the Cu-Mn (*3*), and In-Tl (*4*) systems. Examples of pure metals which undergo martensitic transformations are Co (*5*), Li (*6*), U (*7*), Ce (*8*), and Na (*9*).

The martensite transformation is essentially a crystallographic phenomenon and is not expected to depend on metallic properties. Hence, instances of its occurrence in non-metallic systems should not be rare.

However, since solid phase transformations in oxides and salts have not been studied as extensively as they have been in metals, very few reactions have been identified as martensitic in non-metallic systems. Transformations in $NaNiO_2$ (*10*) and in ZrO_2 (*11*) are martensitic, and one in CsCl (*12*) may perhaps belong in this class also. The occurrence of a martensite transformation in ZrH_2 is still controversial (*13*). It appears that the field of martensite reactions in other than metallic

systems is almost unexplored, and it may be timely to draw attention to their distinctive properties and to discuss the applicability of the phase rule to them.

Properties of Martensitic Transformations

A number of excellent and detailed discussions of the martensite transformation can be found in the literature (*2*, *14*, *15*). For our present purposes, a summary of typical martensite characteristics will suffice. It will be mentioned only in passing that there are a number of so-called atypical or isothermal martensite reactions, e.g., the bainite transformation in steel (*16*), and some of the transformations in uranium and uranium alloys (*7*). However, these isothermal martensite reactions are merely intermediate in character between a conventional phase reaction and the typical martensite transformation to be described below.

While a conventional phase change occurs at a single definite transformation temperature in a pure material, and across a compositional two-phase region in a binary phase diagram, a martensite transformation, in pure or multicomponent materials alike, occurs over a range of temperatures with co-existence of the two phases. The latter are identical in composition, differing in crystal structure only.

For a given specimen history and a given set of experimental conditions, there is for each temperature within the transformation range of a martensite reaction a definite ratio of the amounts of the two phases. This ratio is established almost immediately and does not change with time if the temperature is held constant, and herein lies the distinction from an ordinary non-equilibrium condition. In other words, while a conventional phase change will run its course isothermally at a finite rate, the martensite reaction does not proceed isothermally but only while the temperature is changing, and then it does so with speeds approaching the velocity of sound in the medium. This speed does not diminish at low temperatures, and in fact, it is impossible to inhibit a completely typical martensite reaction by quenching. An atypical or "isothermal" martensite transformation does proceed isothermally but only to a limited extent. It still requires a temperature interval to run its full course.

The identity of composition of the two phases and thus the absence of a two-phase region in a binary phase diagram, is a consequence of the fact that the martensite transformation is diffusionless.[1] This term is defined here to mean that an atom can move only through less than an interatomic distance. Atoms do not move past their neighbors as they do in a conventional nucleation-and-growth process, where atoms migrate to new positions, in order there to build up the structure of the new phase. Thus, the change in crystal structure brought about by the martensite reaction is not "reconstructive" but "displacive," the new structure being a kind of distortion of the old one. It is not surprising then, that mechanical distortion (e.g., by cold-working), which involves shear stresses, can initiate at room temperature a martensite reaction that naturally occurs at sub-zero temperatures, e.g., in 18–8 Cr-Ni stainless steel (*2*). Furthermore, it is found that the crystallographic planes of the martensite phase[2] bear a definite orientation relationship to planes of the parent phase, a subject that has received much study (*4*, *14*, *15*).

A martensite transformation often commences with the sudden "springing-into-being" as it were, of lens- or needle-shaped martensite nuclei throughout a volume of the parent phase. Subsequent growth of the martensite regions is usually limited, and the reaction proceeds primarily by a multiplication of the number of such needles. These martensite nuclei are regions in which the crystal planes are tilted with respect to those of the parent phase, and a grain which was smooth before the transformation often has a stepped appearance afterwards. The phenomenon is frequently accompanied by extensive twinning which—under the polarizing microscope—presents the appearance of alternating light and dark bands traversing the grains that have undergone the martensite transformation.

Martensite reactions exhibit hysteresis when going through a temperature cycle, and the temperature range of the transformation, with respect to both its position and extension along the temperature scale, depends somewhat on the thermal and mechanical history of the specimen.

In the past, the largest number of martensite reactions has been observed in supercooled, i.e., metastable, phases. When the temperature is too low to permit the diffusion necessary for the production of the equilibrium phases by the conventional "nucleation and growth" process, a part of the excess free energy can be eliminated by an alternative, viz., a martensite transformation. Usually, the martensite phases are still metastable with respect to the equilibrium phases and have no region of true thermodynamic stability of their own. To put it in another way: The free energy of martensite is lower (i.e., more negative) than that of the parent phase, but it is higher than that of the equilibrium phase or phases whose formation has been inhibited or at least greatly slowed by quenching. It seems, however, that there are some cases of polymorphic phase changes, normally proceeding by a conventional nucleation and growth process, where quenching of the high-temperature phase leads to replacement of the normal mechanism by one having martensitic characteristics but leading to the same equilibrium phase instead of a metastable martensite phase (*17*). Finally, there are cases, especially in pure metals or compounds, where the martensite mechanism appears to be the only known mode of conversion between two or more different stable crystal structures.

Theories of the Martensite Transformation

Theoretical treatments of the martensite transformation are based on considerations of strain and surface energies (*7*, *19*, *20*, *21*). The semi-quantitative discussion by Knapp and Dehlinger (*21*) is especially illuminating. Their ideas are restated in a greatly simplified qualitative manner by Klepfer and Chiotti (*7*). According to them, martensitic behavior results when the formation of the new phase occurs in such a way as to set up a large strain energy. This increases with the increasing quantity of the new phase and opposes the

[1] For a non-martensitic diffusionless transformation, see (*22*).

[2] A martensite phase—often simply called martensite—is any phase produced by a martensitic mechanism from a higher-temperature phase. The latter is called the parent phase.

conventional thermodynamic driving force for the transformation. Eventually, it will cancel the driving force so that the reaction stops. Lowering the temperature increases the driving force, so that the reaction will proceed until the strain energy has been increased by an equal amount. This point of view apparently can account for the existence of a transformation range and the failure of the reaction to go to completion isothermally. It is not intended here to go into the theories more fully; suffice it to say that they successfully account for many of the special features of martensite transformations, in a few instances in quantitative agreement with experiment.

These theories also point to the origin of the extra degree of freedom that a martensitic system is found to possess, as explained in the next paragraph, and this enables us to reconcile the martensite reaction with the phase rule.

Application of the Phase Rule

In the case of a pure material, the existence of a transformation range for martensite reactions, i.e., a variable instead of a fixed temperature, rather obviously implies one more degree of freedom than the phase rule predicts. This would seem to be true also of multicomponent systems, although it is less obvious there. The case can be argued in a number of ways. The author prefers to recall the fundamental phase rule definition of components. As stated by Ricci (*1*), "this is the smallest number of composition terms (not necessarily individual, single chemical species) capable of independent variation as to proportion in the system, and necessary for the (algebraic) statement of the composition of all the phases in the equilibrium." Since the phases involved in a typical martensite transformation are of identical composition, regardless of the chemical complexity of that composition, it would seem that the number of components, as defined here, is always one, so that the systems which synthetically are multicomponent ones are unary systems in the phase rule sense as far as the martensite transformation is concerned.

It will be recalled that the general form of the phase rule is $F = C - P + n$, where n is the number of intensive variables of which the state of the system is a function. In most instances, $n = 2$ suffices, the two being temperature and pressure. (In open, condensed, systems, of low vapor pressure, the vapor is not counted as a phase, and the pressure is assumed constant, so that $n=1$.) However, whenever the state of the system is found to depend on other variables as well, these must be included in n or the phase rule will not properly describe the behavior of the system. To cite just one example from the literature, in an application of the phase rule to a superconducting system (*18*), the variables were taken as temperature and applied field.

The strain energy, or, in some versions, the sum of strain and surface energy (*7*, *21*) is clearly an intensive variable controlling the course of a martensite transformation and must be included in the phase rule description of the latter. The term n in the phase rule is thus increased to three in the general case or to two in condensed systems, and this furnishes the extra degree of freedom so obviously called for by the behavior of the martensite transformation.

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A modern turbojet engine consumes about one pound of fuel per hour for every pound of thrust. An advanced bomber, such as the B-58 "Hustler" with four turbojet engines, would burn up about 48,000 lbs. of fuel per hour.

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A Semiautomatic Polarograph:

A low cost instrument for student use

Since polarography and instrumental methods, in general, are being introduced into analytical chemistry courses, it is desirable to design a low cost polarographic instrument incorporating the following features: The precision of the instrument should be high enough to make it useful in introductory analytical chemistry but not necessarily in research. The components of the instrument should be readily available at reasonable prices, and it should be possible to assemble them with minimum difficulty. Some degree of automation is desirable. It should be possible to connect the instrument to a recorder to make it fully automatic.

Several designs have been suggested for the assembly of available laboratory apparatus for the production of current-voltage curves. In most instances these have been entirely manual although Favre[1] and Hohn[2] report polarographs in which plotting of the current-voltage curve is greatly simplified. O. H. Müller[3] described a manual instrument making use of a slide wire potentiometer as a voltage divider. Later, C. L. Rulfs[4] made a more compact and portable demonstration unit, utilizing several inexpensive electronic parts. Kolthoff and Lingane[5] describe many commercially-produced instruments as well as others mentioned in the literature.

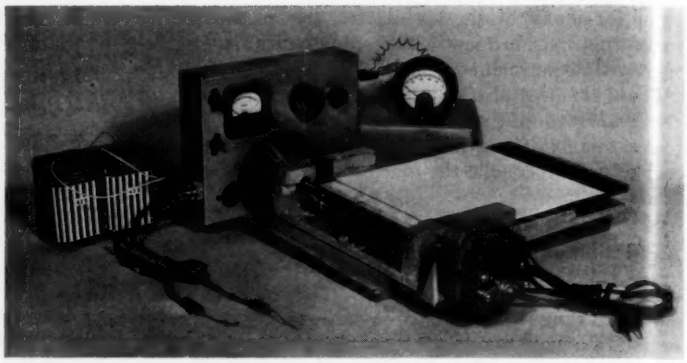

Figure 1. *Parts List:*
1 Simpson dc voltmeter, 0–3 volts, 1000 ohms per volt.
1 Weston dc microammeter, 0–100 microamps, Model 301.
1 Cenco dc microammeter, 0–10 microamps.
1 Beckman helipot, 10 turns, 100 ohms.
1 potentiometer, 100 ohms, 5 watts.
2 switches, toggle, single pole, single throw.
1 socket, 3 prong for cell leads.
4 pin jacks, for batteries and microammeter.
1 motor, Dayton Electric Mfg., Chicago, 1 rpm.
1 rod, 12 in. × $^5/_{16}$-in.
2 bearings, $^5/_{16}$-in. ball.
2 rollers, rubber, $^3/_4$-in. diameter, $^1/_2$-in. wide.
Miscellaneous parts as needed:
8-ft microphone cord.
1 spool of hook-up wire.

Instrument

Simple electric motors with attached gear boxes are available at very low prices since they are mass produced for use in coin-operated machines, etc. A $^1/_{250}$ hp motor geared down to one revolution per minute is very satisfactory. As indicated in Figures 1 and 2, the motor is connected directly to a metal rod, twelve inches long and five-sixteenth inches in diameter, which is supported by two pillow blocks. Two rubber rollers are arranged to press against the rod from below and a sheet of paper can be fed between the rod and rollers. At the end of the rod, opposite the motor, the Beckman precision ten turn helipot, (resistance, 100 ohms, linearity, 0.5 per cent), is mounted, and it is driven by a friction drive from the rod. In this way the helipot and the paper are moved by the rotation of the rod. Therefore, the distance the paper travels will always be proportional to the IR drop measured off by the helipot.

To avoid the use of an automatic cutoff switch, which might fail and allow the high torque motor to destroy the helipot, the helipot is driven by a clamp. This clamp is a clothespin which grips the end of the rod lightly and engages a pin on a disc mounted on the helipot shaft. When the helipot reaches the end of its travel, the clamp slips harmlessly on the rod. The

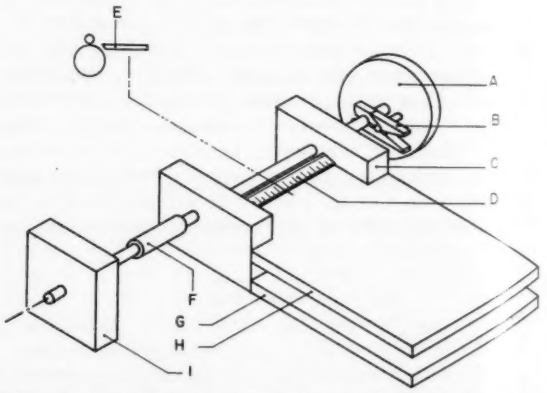

Figure 2. A semiautomatic polarograph. *A.* Disc mounted tightly on helipot shaft and concentric with rod. *B.* Clamp, from clothes pin, used to couple rod to disc so both will rotate together. *C.* One of two bearing blocks which supports the rod. *D.* Scale for plotting microamperes. *E.* Section showing relative positions of paper table, and rod and rubber rollers which feed the paper. *F.* Positive coupling for motor shaft and rod. *G.* Base made of $^1/_4$-in. plywood. *H.* Paper table made of $^1/_4$-in. plywood. Paper slides under scale *D* and is pulled between rod and rubber rollers. *I.* One revolution per minute motor and gear box.

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[5] Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York.

clamp is easily removed so that the helipot can be rotated back to its initial position by means of the disc. Near the rod which rotates and pulls the paper through is placed a scale extending across the paper. For easy reading this scale is marked off in the same way that the microammeter is graduated.

The components used in the electrical circuit shown in Figure 3 can very well be mounted in a small aluminum chassis which may be purchased from a radio supply house. The Simpson dc voltmeter with a 0–3 scale and 1000 ohms per volt resistance is mounted in the chassis and is used to read the voltage span placed across the helipot. The voltage span is controlled by the 100 ohm, 5-watt potentiometer. Two one and one-half volt dry cells supply the necessary voltage. A Weston dc microammeter, scale 0–100, Model 301, and a Cenco 0–10 microammeter are arranged to be plugged in by means of pin jacks. The meter may be removed and an automatic recorder plugged in to make a fully recording instrument. A three-prong jack was mounted in the chassis to provide for the shielded leads from the dropping mercury electrode. This is the same type of socket provided on the Sargent Model XXI Polarograph, and it made it convenient to shift the polarographic cell from our instrument to the Model XXI for comparison purposes.

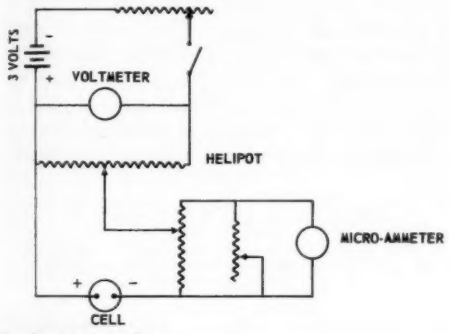

Figure 3. Electrical circuit.

To operate the instrument the usual H-shaped cell is assembled with a dropping mercury electrode, and the sample is added. The battery is connected by means of pin jacks, and the polarity is noted. The desired span voltage is adjusted by means of the potentiometer. Next, the drive clamp is disengaged from the helipot and the helipot is rotated back to zero. The drive clamp is replaced and the instrument is ready to start by switching on the motor.

As the paper moves between the rod and rollers, the readings of the microammeter are plotted directly on the paper at the edge of the scale. There is little time lag as a dot can be made very quickly on the paper at the point on the scale representing the meter reading. The voltage reading, which is proportional to distance on the paper, is plotted automatically since the dot representing microamperes is always placed at the edge of the scale. To finish the polarogram it is only necessary to draw the curve through the plotted points. The whole operation takes little more time than is required for a fully automatically-recorded polarogram. Because of the speed and simplicity of operation, the instrument was used quite satisfactorily with the quantitative analysis class.

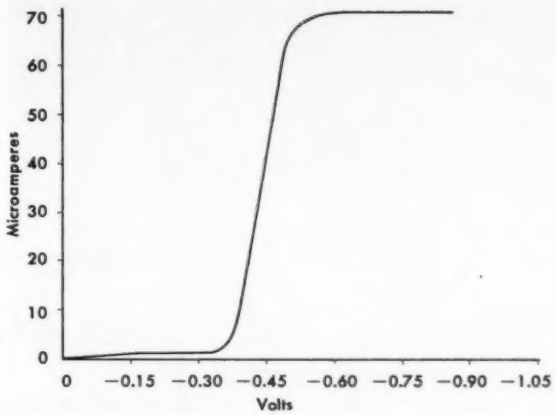

Figure 4. Concentration: 5×10^{-3}M Pb^{++}; Drop rate: 6 sec; Span: 0–1.5 v; Sensitivity: 5 μa/mm.

Results

The instrument produces satisfactory polarograms on one and two component samples. Figure 4 is a typical polarogram obtained by manually plotting only the current component. The calibration curve, shown in Figure 5 obtained from standard lead solutions, shows the feasibility of using an instrument of this type for determinations in quantitative analysis courses.

The paper used in the described instrument is of letter size unless ten complete turns of the rod and helipot are desired. A sheet of legal size paper is long enough to accommodate ten revolutions of the rod.

It is convenient to stop the motor if reading the galvanometer requires more time. Since the paper drive and the helipot are operated by the same rod, stopping and starting the motor had no effect on the polarogram.

The motor used was a very simple, non-synchronous type and, of course, a varying speed does not effect the polarogram as the applied potential and the paper speed are tied together. However, when the microammeter is replaced by a recorder, to make a completely recording instrument, it is necessary that the helipot be driven at a uniform speed. Within the precision of the instru-

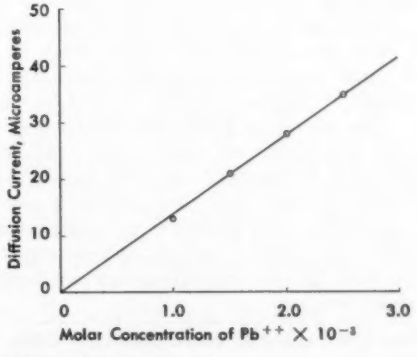

Figure 5. Standardization curve.

ment, the motor is constant speed, probably due to the mechanical advantages provided by its gear box.

All parts of the instrument are exposed, and students using the instrument have an opportunity to observe automation at first hand.

When wide ranges of concentration are to be used, a more sensitive galvanometer with a suitable Aryton shunt is used instead of the microammeters suggested.

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Determination of Reaction Rates with an A.C. Conductivity Bridge

A student experiment

In this paper we describe a quantitative experiment in chemical kinetics which is suitable for advanced freshmen or for a physical chemistry course. It involves a study of the solvolysis of tertiary butyl chloride (hereafter called TBC) by means of conductance measurements.

In all freshman chemistry courses at Yale, certain fundamental ideas concerning rates of reaction are taught. The law of mass action is presented in terms of simple collision theory, and the concept of reaction order in a chemical rate equation is explored. The Arrhenius equation for the effect of temperature on a reaction rate constant is discussed in terms of the distribution of molecular energies, and the idea is presented that only collisions between molecules having energies in excess of some minimum energy, the activation energy, will be successful in terms of chemical reaction. We thought that it would be worthwhile to introduce an experiment to illustrate these ideas into the accompanying quantitative laboratory course.

After examination of available experiments, we came to the conclusion that none of these was of sufficient precision for our purposes. We wanted an experiment which would be cheap enough to permit performance by a number of groups of students, yet accurate and complex enough to be challenging to the students. We were not averse to a measurement of an indirect sort which would involve some manipulation of the data to arrive at the desired constants.

The following experiment was developed and has been successfully tried by students in our freshman honors course. The experiment should also be suitable for a physical chemistry laboratory course since it yields results of good quantitative precision and exemplifies all the points of interest usually covered in chemical kinetics. The resistance measurements used to follow the reaction are performed with a 1-kc transistorized AC bridge which we designed and built for the purpose. The oscillator, bridge, and detector were assembled for parts expenditure of $8.50 per set exclusive of batteries. The philosophy of design and construction is similar to that for the potentiometer we have previously described.[1]

The Reaction

TBC reacts with water according to the over-all equation

$$(CH_3)_3CCl + 2H_2O \rightarrow (CH_3)_3COH + H_3O^+ + Cl^- \quad (1)$$

Of the reactants and products, only hydrochloric acid contributes significantly to the electrical conductivity of the solution, so a measurement of conductance can be used to follow the progress of the over-all reaction. The reaction has been shown to be first order in [TBC]; it is believed that the rate determining step is the formation of a carbonium ion, followed by a fast reaction with a hydroxylic solvent such as water or ethanol.[2]

This mechanism may be represented as follows:

$$(CH_3)_3CCl \xrightarrow[\text{slow}]{H_2O} (CH_3)_3C^+ + Cl^- \quad (2)$$

$$(CH_3)_3C^+ + 2\ ROH \xrightarrow[\text{fast}]{} (CH_3)_3COR + ROH_2^+ \quad (3)$$

Here R is either H or C_2H_5. For this mechanism

$$-d[TBC]/dt = d[HCl]/dt = k[TBC] \quad (4)$$

where k is the first order rate constant for (2). Since

$$[HCl] = [TBC]_0 - [TBC] \quad (5)$$

where $[TBC]_0$ is the initial concentration of the reacting chloride, the rate equation (4) may be written

$$d[HCL]/dt = k([TBC]_0 - [HCl]) \quad (6)$$

This may be integrated to give

$$[HCl] = [TBC]_0 (1 - e^{-kt}) \quad (7)$$

The conductance of the solution is identical to $1/R$, where R is the measured resistance, and

$$1/R = K_1[HCl] + K_2[X] \quad (8)$$

In this equation K_1 and K_2 include the cell constant and mobilities of the ions, and $[X]$ is the concentration of any impurity ions in solution. It is at this point that a Guggenheim analysis[3] is performed to extract k from the data without having to evaluate the cell constants, $[TBC]_0$, $[X]$, or the ionic mobilities. It is pointed out to the student that this is typical of

[1] Chesick, J. P., and Patterson, A., Jr., J. Chem. Educ., 36, 496 (1959).

[2] Streitwieser, A., *Chem. Rev.*, 56, 571 (1956).

[3] Robertson, R. E., *Canadian J. Chem.*, 33, 1536 (1955)

the juggling an experimental scientist will do when he can avoid unnecessary work.

Solve (8) for [HCl] and substitute into (7).

$$1/K_1R - K_2[X]/K_1 = [\mathrm{TBC}]_0(1 - e^{-kt}) \qquad (9)$$

Now evaluate (9) for $R = R_{t+\delta}$ at the time $t+\delta$, and for $R=R_t$ at time t, where δ is a constant increment of time. Subtract the second evaluation of (9) from the first and multiply the resulting expression by K_1.

$$\begin{aligned} 1/R_{t+\delta} - 1/R_t &= K_1[\mathrm{TBC}]_0(e^{-kt} - e)^{-k(t+\delta)} \qquad (10) \\ &= K_1[\mathrm{TBC}]_0(1 - e^{-k\delta})e^{-kt} \end{aligned}$$

Note that this has eliminated $[X]$ and K_2. On taking the logarithm of (10), the result is

$$\ln(1/R_{t+\delta} - 1/R_t) = -kt + \ln\left\{K_1[\mathrm{TBC}]_0(1 - e^{-k\delta})\right\} \qquad (11)$$

A plot of $\ln(1/R_{t+\delta} - 1/R_t)$ versus t will be a straight line of slope $-k$ since δ is constant throughout the calculations for a given run. The exact value of δ used is somewhat arbitrary, although best results are obtained if it is about one half life. Since k can be obtained by this method without explicitly evaluating K_1 or $[\mathrm{TBC}]_0$, the conductance (reaction) cell may be of simple construction. All that is required is that the electrodes not be disturbed during the course of a run. Initial reactant concentrations need only be measured accurately enough to insure that the final resistances of the solution lie in a convenient range of the bridge.

By making runs at different temperatures the student can evaluate the activation energy from a plot of $ln(k)$ versus $1/T$. Here all that is required is that the relative temperature measurements be good to a few tenths of a degree. The absolute error in T may be much greater than this. We used -15°C to $+50$°C thermometers graduated in degrees which could be estimated to ± 0.1°C. No absolute calibration of the thermometers should be necessary since one is most interested in relative values of T.

The Experiment

The materials needed are: a 100-ml graduate, a 10-ml graduate or pipet to measure 1 ml of solution to $\pm 20\%$, two 400-ml beakers, two 50-ml beakers, a stirring rod, a thermometer with cork for support (see preceding section for requirements of thermometer), an electrode assembly (to be described later), an a.c. resistance bridge accurate to better than 5%, (to be described later), a one pint wide-mouth thermos jug for a constant temperature bath with a fiberboard lid cut out for the reaction beaker and thermometer, 95% ethanol, and a stock solution of tertiary butyl chloride in absolute ethanol of about 0.15 F. A means of time measurement is also required (large electric clocks with sweep seconds hands, or wrist watches with sweep second hands). The stock chloride solution should probably be kept in a refrigerator until ready for use since there is some residual water in most "absolute" alcohol which would promote a rather slow solvolysis in the stock solution. Figure 1 shows the equipment used in the measurements.

Since the reaction proceeds too rapidly for convenience in pure water near room temperature, a solvent mixture of 100 ml of 95% ethanol and 120 ml of distilled water is used. The thermos is filled almost

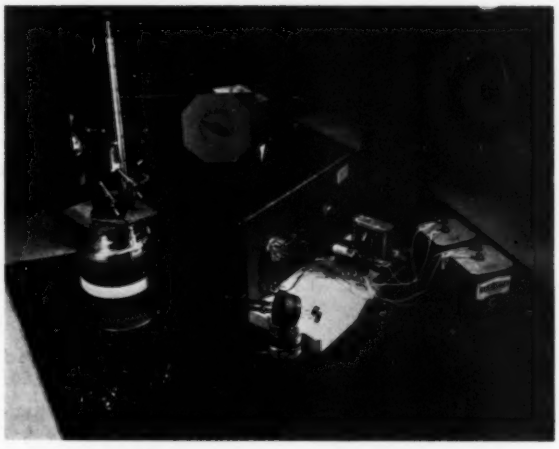
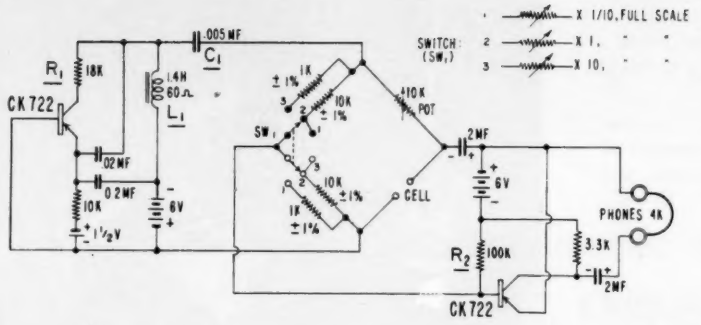


Figure 1. A.C. bridge, conductance cell, and thermostat assemblies.

completely with water of the desired temperature; 30 ml of solvent mixture is placed in the 50-ml beaker used as a reaction vessel; and the beaker and thermometer are suspended by the fiberboard lid in the thermostat to come to thermal equilibrium. The second 50-ml beaker is used to support the electrodes while the first beaker is being rinsed or filled. The electrode assembly is placed on the beaker at this time to aid equilibration with the bath and to insulate the surface of the beaker. Reaction is started and time is counted when 1 ml of the stock solution is added to the beaker in the bath. The electrodes are replaced, the bridge leads are connected, and resistance measurements are begun. The time of balancing the bridge is noted, and *then* the resistance reading is taken. Suggested temperatures for three runs are 20°C, 27°C, and 35°C. Resistance readings should be made every minute at the lower temperatures and oftener if possible at the highest temperature while the resistance is changing rapidly. The reaction should be followed for 40 minutes, 35 minutes, and 20 minutes if the experiments are performed at the suggested temperatures. The temperatures are read at the beginning and end of each run. The temperature should not drift more than a few tenths of a degree in the course of a run since the suggested temperatures bracket room temperature and the thermos jug is a good thermostat. If another temperature range is used, the solvent mixture may be adjusted to give convenient reaction rates.

A plot of the conductance, $1/R$, versus time is made for each on a sheet of graph paper. A smooth curve is drawn through the data, and points are read from this curve to construct the graph of $\ln(1/R_{t+\delta} - 1/R_t)$ versus time. From this second graph the value of k is determined. Students need not bother with natural logarithms if they are informed of the conversion between bases e and 10. Suggested values of δ are 1000 sec, 800 sec, and 400 sec for the three temperatures. Time should be increased by about 100 or 200 seconds for each point in the log plot. The plot of $\ln k$ versus $1/T$ is then made to determine the activation energy. The experiment has been successfully performed by students in a three-hour period. Runs at different temperatures may be performed on different days if the solvent mixture used by the student is



A.C. Bridge Parts List

2–Raytheon CK722 transistors
1–1.4 h, 60 ohm inductance, such as Lafayette TR-33
2–2 μf electrolytic capacitors, such as Lafayette CF-120
1 each–0.2, 0.02, and 0.005 μf capacitor
1 each–10, 18, and 3.3 K ohm carbon resistor, ±10%, 1/2 w
2 each–1 and 10 K ohm deposited carbon resistor, ±1%, 1/2 watt, such as Aerovox Carbofilm
1–10 K ohm carbon potentiometer, such as Allen Bradley Type J
1–2 pole, 3 or more position nonshorting selector switch, such as Mallory 3226J
1–4 K ohm headphones, such as Lafayette F-374
2–6 v batteries, such as Burgess Type F4H
1—1½ v battery, such as Burgess Type NE
Alligator clips, Fahnestock clips, bar knob, wire, sheet copper, screws, etc.

Figure 2. Circuit diagram for audio frequency student conductivity bridge. The value of R_1 depends upon the Q of L_1; if R_1 is too big, oscillation stops; if R_1 is too small, the sine wave is clipped. The maximum value of C_1 is determined by the load the bridge places on the oscillator; if C_1 is too large—around 0.01 μf for the values shown—oscillation stops. On some of the units built with unselected components, it was found better to remove R_2 for maximum signal output.

saved in a stoppered bottle and if the student uses the same thermometer each time.

The A.C. Bridge

An a.c. resistance bridge must be used to avoid polarization effects. Figure 1 shows front and back views of the bridge we produced, and Figure 2 shows the circuit diagram. The chassis consists of a wood base and a Masonite front panel. The ratio arms of the bridge are ±1% resistors which are selected by the two-pole three-position range switch SW_1 to change the full scale reading of the resistance dial by factors of ten from 10^3 to 10^4 to 10^5 ohms. The oscillator provides a signal of approximately 1 kc frequency which is applied to the bridge. The off-balance signal from the bridge is fed into a one-stage transistor amplifier and then detected by a pair of inexpensive earphones. Silence, or a minimum in the sound heard in the headphones, indicates that the bridge is balanced. Standard radio parts are used; since the transistors are low voltage devices, the cheapest low-power parts available may be used. The maximum value of C_1 is determined by the load the bridge places on the oscillator. If the C_1 is too large, the oscillator will be severely drained and will cease operation. The value of R_1 depends on the Q of L_1. If R_1 is too big, oscillation stops. If R_1 is too small the wave will be clipped. The parts listed in the parts list and on the circuit diagram gave generally good results in the construction of ten of these sets, but since the low-cost transistors and components may not all be alike, some experimentation may be needed.

The 10 K potentiometer dial must be calibrated after the bridge is assembled. This was done by comparing the bridge with a standard decade resistance box. The correct dial position for each 500 ohms of the potentiometer was marked on the paper cemented to the Masonite panel. The smaller divisions were interpolated by eye. Resistance readings are good to better than ±2% at the high end of the dial; the accuracy falls to about ±5% at the low end. An alternative procedure would be to purchase a 360° potentiometer for each bridge which was linear to better than ±1%. A 360° dial marked off in even divisions could then be used without hand calibration. This would add about $2.60 to the cost of each unit. The ordinary carbon potentiometer used in our units definitely was too non-linear for use without calibration. Wire-wound potentiometers are not suitable since they do not allow fine positioning of the knob.

Electrode Assembly

The actual electrodes are pieces of 0.005-in. thick platinum sheet of area about 1 cm^2. These sheets are forged to short lengths of #26 gauge platinum wire. The free end of the platinum wire is soft soldered to a copper lead wire, and a soft glass tube is sealed around the platinum wire near the electrode plate. A pair of these electrode assemblies is slid through the holes in a #9 two-hole rubber stopper, so that the bottom of the electrode plates will come near but not touch the bottom when the stopper is placed in the 50-ml reaction beaker. The outer ends of the copper lead wires are then wound around the glass tubing leaving an end for the attachment of clip leads from the resistance bridge. The use of vacuum wax is advisable to hold the copper wire in place to avoid breaking the platinum wire. See Figure 1 for illustration of the final assembly. It was found necessary to platinize the electrodes lightly in order to get a decent balance of the bridge with the dilute HCl solution used in the measurements. Although the cell constant of this electrode system will certainly change with flexing of the glass tubing in the rubber stopper and with slight distortion of the thin electrodes, this will not matter if the electrodes are not disturbed during the run, since the analysis of the data eliminates the cell constant.

Results

Sets of data were obtained by thirteen pairs of freshmen who performed this experiment. Since the thermometers were not calibrated on an absolute basis, it is not possible to compare values of individual rate constants, but the activation energies determined from the Arrhenius plots may be examined for consistency. The average activation energy obtained in thirteen determinations was 19.1 kcal/mole.

This compares favorably with the literature value of 21.0 kcal/mole for similar solvent and temperature condition.[4] The standard deviation of the student determinations from this value was 3.0 kcal/mole.

The student response was in general favorable; in some cases the students were quite enthusiastic. One student commented that he appreciated the opportunity to combine his chemistry, mathematics, and physics in one operation.

The use of the bridge in resistance measurements seemed to present no serious problem to any student. While the bridge was capable of being operated as "black box," circuit diagrams and explanations were provided for those interested.

The Guggenheim analysis for extraction of rate constants from the data was evidently adequately presented to the students. Few questions were asked on this operation, and few errors appeared in this part of the calculations. Excellent linear Arrhenius plots were obtained by about half the students. Some scatter in the data of the other half indicated that care is needed in measurement of temperatures and in attainment of thermal steady state in the bath and beaker.

Acknowledgment

We wish to thank Dr. J. B. Hyne for his advice and suggestion of reacting system.

[4] Winstein, S., and Fainberg, A. H., *J. Am. Chem. Soc.*, 79, 5937 (1957).

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Philosophy and Carbohydrate Chemistry

When chemists are told that they have been using philosophy all the time, they are as surprised, although not so genuinely pleased as Molière's Bourgeois Gentilhomme, the Would-be Gentleman, when he was informed that he had been using prose all the time. These chemists will be displeased because they see in philosophy only a discordant struggle with ill-defined words, with unjustifiable questions and arbitrary answers. That, however, is not a true picture of philosophy. In simplest words, it can be defined as the search for understanding based upon a system of meanings. This search requires a constant checking of the system for consistency in itself and for correspondence with experience. In the laying of foundations, as by the atomic theory, or in the erection of frameworks, as with the laws of conservation, philosophy is always involved in science and, reciprocally, science uses philosophy.

One way toward recognizing this important relationship, and perhaps the best for the non-speculative mind, is to consider a highly developed field in a special branch of science. Carbohydrate chemistry is selected here because it is close to the author's own efforts in chemistry. A study of the relationships between philosophy and carbohydrate chemistry may prepare for a clearer understanding of the fundamentals and stimulate ideas for future applications.

Philosophy has provided carbohydrate chemistry with its basic concepts. In historical order, they are: dualism and polarity, the formalism for reaction rates, the model of molecular structure in space and asymmetry as its consequence. These concepts have been the subject of much discussion in philosophy, and their scope is wide enough to be used in many sciences. Some reference to this wide scope will be necessary while tracing their use in carbohydrate chemistry.

Dualism and Polarity

In the evolution of chemistry, dualism took several specific forms. In connection with the present theme, two discoveries are especially pertinent; one concerned the nature of the salts, the other the theory of combustion. Dualism did not enter here as a deliberate effort to invoke the help of an old philosophical idea. Instead, new experimental results formed the start. They had to be explained, and the attempt to do that just naturally resulted in dualistic theories. They were felt to be successful explanations because they connected the new experiences with philosophically well prepared fundamentals.

Presented before the Division of Carbohydrate Chemistry, at the 135th Meeting of the American Chemical Society, Boston, April 6, 1959.

For a long time, almost anything that can occur in crystal form was called salt. In the latter part of the 18th century, a new definition was developed. Acids are the chemical opposites of bases; when the two combine, they form a neutral product, now defined as being a salt. Somewhat later, Hegel, the proponent of "natural philosophy," published his dialectic system in which thesis and antithesis finally combine to synthesis. This is essentially the same tripartite arrangement, based upon dualism, as is contained in the new theory of salts. Yet, neither referred to the other for confirmation. It was not necessary; both were derived from the same philosophical concept.

The new theory of combustion consisted in a reversion of the phlogiston theory (*1*). Oxygen took the place of phlogiston by reversing the plus or minus sign. The dualism that had remained dormant in the old theory became a pronounced part of the new one. It was the dualism between the oxidizable substances and the general oxidizer, oxygen.

Both dualisms, that of acids and bases, and the one between oxidizables and oxidizer, remain with us. They have become convenient simplifications, and they were fortified, very soon after their formulation, by the electrochemical concepts of polarity. All our explanations in carbohydrate chemistry are firmly based on these two kinds of dualism and polarity. They had been prepared in philosophy as scientific possibilities; they were intrinsically accepted, tested, and found to be consistent with a wide range of experimental results.

Reaction Rates

In theories using dualism and polarity the philosophical vein may be easily seen; it is more difficult to do the same in the formulations of reaction rates. Here, dualism is supplanted by the unitary law of mass action. Somewhat vaguely foreseen by Berthollet in the first years of the 19th century, this law was actually formulated about fifty years later, and that occurred a few years after it had already served in the first mathematical expression for a reaction rate. In 1850, Ludwig Wilhelmy proposed that the progress of sugar inversion with time might be presented by the formula:

$$-\frac{dZ}{dT} = MSZ$$

where Z (Zucker) stands for the sugar concentration, M and S designate something like unit-rates and the acid S (Säure) used. Practically speaking, MS can be considered a constant in a particular experimental

arrangement, so that the formula becomes

$$-\frac{dZ}{dT} = kZ$$

k = constant. Wilhelmy did not derive his formula from any measurements; he started with the formula and then tested it for conformance with the observed facts. With confidence, he built upon a philosophically prepared foundation, and he was not disappointed.

In a similar manner, the same foundation had actually been used a few years earlier, and it is not certain whether Wilhelmy knew about this. Ernst Heinrich Weber in Leipzig had suggested a formula for connecting the just noticeable difference in sensation with the change dR of the stimulus (Reiz) R:

$$dR = cR$$

c = constant. Fechner improved this by expressing the liminal increment of sensation as dS and thus completing the mathematical form (*2*):

$$\frac{dR}{dS} = cR$$

About a third of a century later, van't Hoff in Amsterdam declared: "Experience will show that in the described case (of dibromo-succinic acid) there is proportionality between the transformable quantity and the transformed quantity" (*3*):

$$\frac{dC}{dt} = KC$$

The formalism that was used to explain the rate of a sugar reaction recurred in three different minds at three different times and places. It did so, not because of overwhelming experimental material, which in fact was very scanty, but because of the value placed upon a general idea. The metaphysical extension of this idea to end-causes and teleology was completely left aside when only the proportionality between the quantities, the transformable and the transformed, was significant and useful.

The Carbon Model and Asymmetry

Relationships to philosophy appear in science not only in special expressions of general doctrines, like dualism or mechanism, but also in the construction of models far exceeding the experimental basis. Van't Hoff constructed such a model after he had been thinking about the problem of the isomeric lactic acids, these products of sugar conversions. Johannes Wislicenus had just (1873) shown them as represented by the same chemical formula, $CH_3CHOHCOOH$. While taking a walk, to relax from his studying, van't Hoff conceived his proposal "to extend the structural formulas of chemistry into space (*4*)." At that time he was 22 and a student! Immediately, he brought his general idea into specific form.

The simple model of a tetrahedral arrangement around the carbon atom has been unbelievably successful. We use it to derive models for all carbohydrate reactions and isomerisms. Electron spectroscopy and X-ray diffraction measurements lead to more elaborations, all consistent with the original concept. The rather crudely mechanical concept of the valence angles, as well as the highly refined conformational analysis of boat and chair forms, is based on the tetrahedron model. Dualism enters the picture in the form of the two asymmetric isomers which turn the plane of polarized light to the right or to the left.

Carbohydrate Research and Philosophical Questions

The three philosophical aspects described so far are concerned with carbohydrate chemistry, but they are not limited to it. The dualistic scheme for salt = acid + base recurs for glycoside = aglycon + sugar, or enzyme = coenzyme + apoenzyme, to which biological research has added organizer = co-organizer + apo-organizer. The proportionality between the transformable and the transformed was also found valid for radioactive decay, when Rutherford and Soddy (*5*) formulated the rate of decay as

$$\frac{dN_t}{dt} = -\lambda N_t$$

N_t = number of unchanged atoms at time t, and λ = disintegration constant. The question remains whether there are philosophical relationships that are characteristic for carbohydrate chemistry alone.

The old philosophical chemistry sought complete explanations, but it found them only in identities. A substance was an oil because it contained the principle of oiliness. We have learned to avoid identities as a short cut to completeness. Instead, we try to explain through wide spanned connections. In the context of carbohydrate chemistry, a good example can be seen in the fact that Emil Fischer advanced knowledge in this field by bringing into it his phenylhydrazine, the result of an entirely different study on a derivative of what he was the first to call hydrazine (1875). Through the synthesis of new carbohydrate compounds, the hydrazones and the osazones, he opened a highly productive period in carbohydrate chemistry.

In this sense of a limited philosophy through wide connections between different experimental results, much remains possible and to be done. With great experimental skill, carbohydrate chemists have expanded our knowledge by an ever-increasing multitude of special facts. Apparently, the great effort did not leave any energy for building connecting theories on philosophical foundations. We know that broad-leaf plants contain more hemicellulose and xylose in their wood than needle-leaved softwoods. Can we find a connection, not a short cut, between the botanical and the chemical characteristics? Should the way to it lead through a deeper study of the relationships to the methoxyl contents which are lower in the lignin of the softwoods than in hardwoods?

Should we start at lower forms of plant life? The polysaccharides of *Rhodophyceae* are composed of D- and L-galactose (e.g., agar, carrageenan), whereas *Phaephyceae* contain 3-O-methyl-L-fucose, as in fucoidin of the brown algae *Fucus veseculosus*, and other brown algae, like *Laminaria*, have mainly D-glucose saccharides (*6*). The experimental work that brought this to light is admirable; may we now permit a little philosophical wondering about meanings and connections? It will lead to more ideas for further research.

The blood-group substances contain glucosamine, galactosamine, galactose, and fucose; the proportions of galactose to hexosamine are 0.6 for A-substance;

1.2 for H-substance; 1.5 for B-substance (*7*). In a philosophical vein, one would ask about relationships to the carbohydrates in heparin, the anti-clogging substance for blood.

The examples could be multiplied many times. The philosphical wondering about finding an otherwise rare carbohydrate, ribose, in the nucleic acids, or sulfates in some polysaccharides when otherwise phosphates are so prominent, can at least enliven the study of carbohydrate chemistry. Such wondering would not be satisfied by completeness achieved through identities. An example would be to try to explain the fact that the polysaccharides of grasses are chains of fructo-furanosides because of the essential "nature" of grass. On the other hand, the search for the specific completeness in limited systems could help in actual, experimental situations. An example for that may be quoted in closing:

In 1916, Irvine and Robertson (*8*) discovered that "one form of methyl fructoside evidently possesses in a marked degree the property of combining with acetone, even to the extent of abstracting the residual traces of the ketone present in the 'acetone-free' methyl alcohol used by Purdie and Paul." The authors concluded that methylfructoside could be used to remove the traces of acetone from methyl alcohol. However, when they carried out the methylation with the methyl alcohol "thus deprived of . . . acetone," the condensation reaction was abnormal. A few years later, Menzies (*9*) showed that after such treatment, the methyl alcohol contained water from the previous reaction, so that the abnormal "behavior described by Irvine and Robertson is to be attributed, not to the elimination of acetone, but to the introduction of water into their recovered alcohol." Had the attention of Irvine and Robertson in their elegant investigation not been limited to the new acetone compound, but extended to the complete events in its formation, the error in neglecting the other part of what they did to the methanol would have been avoided.

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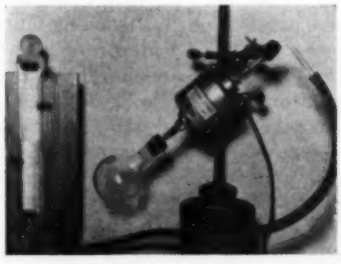
A Simple, Inexpensive Rotary Film Evaporator

During the past few years the technique of film evaporation has become increasingly popular as a means for the rapid removal of solvent. The simple and inexpensive arrangement shown in the figure may be extemporized rapidly from standard laboratory equipment by replacing the shaft of a hollow-spindle stirrer with a glass tube terminating in a ball-joint at its upper end and a rubber stopper or standard-taper joint at the lower end. When lubricated with mineral oil, the ball joint will hold a good water-pump vacuum (10 mm or less) even while being rotated for extended periods. The glass tube to the upper member of the joint should be bent at an angle so that the condensate will not carry impurities from the suction hose back into the flask.

If a hollow-spindle motor is not available, it is usually possible to adapt equipment at hand, most often by replacing the ordinary solid shaft of an electric stirrer motor by a metal tube of appropriate size. Also, inexpensive, hollow-spindle mounted mandrels are available[1] and may be used powered through a belt-drive to an ordinary stirrer motor. For multiple evaporations a number of such mandrels may be run in series by belt drives from a single motor, the solvent being removed through a vacuum manifold attached to the water pump.



As well as being cheap and very easy to construct, the equipment is simple to clean, has no metal parts that may be attacked by evaporating vapors, and may be taken apart immediately so that the motor is not kept idle for extended periods in an expensive permanent set-up. In the writer's experience, it is considerably easier to make and holds a steady vacuum more reliably than the device suggested by Greef and Larsen.[2]

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A. W. Hofmann and the Founding of the Royal College of Chemistry

Spring, 1845, found August Wilhelm Hofmann at twenty-eight in his first year of teaching at the University of Bonn with the title of *Privatdozent* (unsalaried instructor). Behind him were happy, fruitful years of graduate study at the University of Giessen, where under the tutelage of the renowned Liebig he had already discovered the presence of aniline in coal tar and, by studying the properties of the chlorine derivatives of that base, lent support to Dumas' and Laurent's substitution theory as against the theory of electrical attraction which Berzelius insisted also applied to organic compounds (*1*). Just as he was about to settle into an academic routine, he received an offer to teach in London. This proposition was so favorable that it was impossible for him to resist. He was approached about this position by Sir James Clark, private physician to the Queen, who was a leading figure in a private society which had just been founded in London for the purpose of establishing a school devoted exclusively to the teaching of chemistry.

England's First School of Chemistry

The idea of creating such an institution can be traced back to 1842 when Liebig made a triumphal tour of the island. At that time the celebrated chemist was lionized by British colleagues, manufacturers, and in particular by the landed gentry who were captivated by his eloquent testimony on the usefulness of chemistry to agriculture. They had just commissioned him to write his celebrated "Chemistry of Agriculture and Physiology," and were eager to put his teachings into practice on their estates (*2*). The widespread enthusiasm for chemistry first found its expression in the opening of a chemical laboratory at the School of Mines. The universities, too, gave increased attention to laboratory teaching, yet they limited their teaching almost exclusively to inorganic and analytical chemistry. Even more significant as well as undesirable for chemistry itself, was their subordination of that science to professional needs, i.e., the training of engineers and physicians. What was needed was a school exclusively devoted to chemistry and one which could preferably concentrate on organic chemistry.

The governing council of the new school naturally turned to Liebig when it came to suggesting a suitable head. When he suggested Hofmann they charged Sir James with negotiating with the young professor. The interviews were conducted during August of 1845, while Sir James was on a trip accompanying Queen Victoria and Prince Albert on a Royal visit to the Prussian Rhineland (*3*). The Prince took a personal interest in the matter. He and the Queen even paid a visit to Hofmann's private apartment which by coincidence had been the very suite of rooms he had occupied a decade earlier while himself a student at the University of Bonn. It is reported that Hofmann ingratiated himself with his Royal visitors by entertaining them with a few chemical demonstrations (*4*).

After a month of feverish preparation, Hofmann and his German assistant, Herman Bleibrtreu, were able to greet the first twenty-six students on schedule in hastily-equipped laboratories located in a rented building on Hanover Square. The immediate success of Hofmann's teaching gave the council heart to launch at once a fund-raising campaign to erect a permanent laboratory building to the rear of the temporary laboratories, and fronting on Oxford Street. The drive being successful, the cornerstone was laid by Prince Albert on June 16, 1846, and by the start of the fall semester it was ready for occupancy (Fig. 1). The vigor with which the college was launched augured well for a brilliant future.

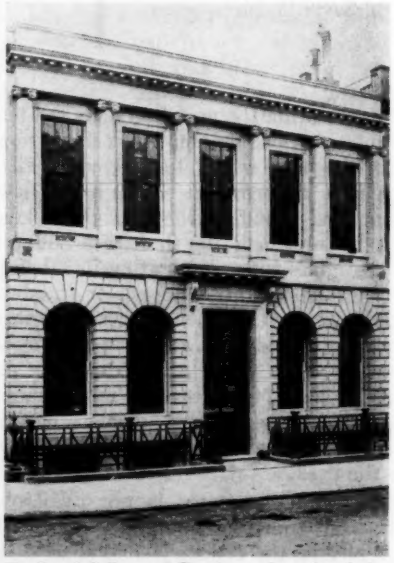

Figure 1. The Royal College of Chemistry whose foundation stone was laid by Prince Albert on June 26, 1846.

But it was not to be. Not only did interest flag, as it so often does after a building program is successfully terminated, but also the years 1846–48 were lean, taxing the generosity of wealthy donors to the limit. Further-

[1] This article has been adapted from the author's recent book, "The Emergence of the German Dye Industry," University of Illinois Press, 1959.

more, a number of supporters became disenchanted with the college when Hofmann, for lack of time and facilities, declined their request for free analyses of such things as soil samples—a service which they had been led to expect from the promotional literature of the initial fund drive. The governing council now had to make the decision either to honor this promise and otherwise to expand the service of the college to the wider community, or to retrench and limit expenditures strictly to chemical research and instruction. After failure to secure financial help from the government, it was decided in favor of the latter. Tuition fees also were raised, and property to the rear of the newly-built laboratory, which had been earmarked for future expansion, was sold (*5*).

Only a precarious financial equilibrium was attained through these measures. Hofmann, Sir James, and others deeply committed to the college found the perpetual worry over money so irritating that they kept pressing the indifferent government for help. Finally, in 1852 they succeeded. A vacancy occurred in the School of Mines when its chemist, Lyon Playfair, accepted a professorship at Edinburgh, and it was decided to appoint Hofmann as his successor while at the same time merging the Royal College of Chemistry with the School of Mines to form a subdivision of the Museum of Practical Geology. Though the college was now financially secure, the change was not altogether for the good, for it was now in danger of becoming a mere service department to a geological institution. While Hofmann remained head of the laboratory, (Fig. 2) he fought successfully to preserve its identity as a school for training research chemists. However, soon after he decided to leave England in 1865 to become head of the chemical institute of the University of Berlin, all vestiges of independence of the former college disappeared one by one—its teaching and research program gradually losing ground to the universities where science at long last took firm root in the 1870's (*6*).

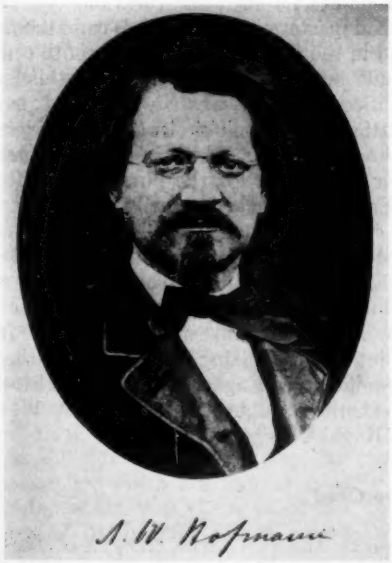

Figure 2. Hofmann as he appeared while Professor of Chemistry at the Royal College, about 1860.

Despite the adverse forces which dogged the fate of the college during its entire history, the school became surprisingly influential and creative under Hofmann's leadership. For this success Hofmann himself gives ample credit to such devoted council members as Sir James Clark and Lord Ashburton, but it was his own remarkable skill at gaining the support and friendship of these patrons which kept them actively interested in the college's welfare. He was as capable an administrator as he was a researcher and teacher; and these qualities, combined with his social talents gained him much respect throughout London society (*7*). The size and range of his circle of acquaintances and friends grew to be quite astonishing. Dinners, speeches, parties, conventions, so often burdensome to intellectually creative people, were occasions of enjoyment and relaxation for the affable Hofmann, who often combined business with pleasure. His capacity for work was extraordinary. No other adjective but prodigious can describe what this young German chemist accomplished in his first year in London. There was the matter of working out a course of study and equipping the temporary laboratories. At the same time plans for the new laboratory building needed lengthy consultation with the council and the architect. Then followed the crisis over the school's finances which was to worry Hofmann for six years. To augment his initially meager salary, Hofmann was obliged to carry out analyses as well as act as consultant for chemical industries and the British government. The additional money was needed to support a family, for in August of 1846 he returned to Germany to marry Helene Moldenhauer, a niece of Mrs. Liebig's and brought his bride back to London. To all this one must not forget to add the effort of settling in a foreign country and learning its language—a task far more time- and energy-consuming than suspected by those who have never done it.

Teaching and Research

Hofmann was a superb teacher. The success of his students attests to that. Many of them went on to gain lasting recognition as organic chemists and chemical manufacturers, most notably of aniline dyes. The comments these students made in later years concerning their training are remarkably alive as well as favorable to their professor. Sir Frederick Abel speaking at the occasion of Hofmann's death in 1892, summed up his teacher's qualifications as follows:

> . . . his success was ascribable to the possession of a happy and rare combination of the highest talents as a teacher with exceptional powers as an investigator, inexhaustible industry and energy, and enthusiasm not to be subdued by any obstacle; a characteristic quality possessed in the highest degree by his great master, Liebig (*8*).

There were, of course, other instructors at the Royal College who taught its sixty-odd students. All of these were carefully picked by Hofmann. Just as did Liebig in Giessen, Hofmann often retained for a few years the services of his ablest graduates as laboratory assistants. Besides these young men, who stood in the full tide of their physical and mental vigor, there came to the college a number of young chemists who were given the rank of either Special Assistant or of Honorary Assistant Professor. Almost all of them were graduates of German universities, some being English, others German. Among them the following are still remem-

bered for their contributions to chemistry: Herman Bleibtreu, David Price, John Blythe, John Stenhouse, Peter Griess, Adolp Kolbe, James Sheridan Muspratt, Otto Witt, Carl A. Martius, and Henry Medlock. Most of these young doctors worked for the college from one to three years before Hofmann got them better paying jobs, usually with British chemical firms. Through them the London school stayed abreast of the latest chemical thinking on the Continent, and with their help the school became for a while the most productive organic chemical laboratory in the world after Giessen.

The research program which Hofmann instituted in London was essentially a continuation of the investigations on aniline which he had begun in Germany. Initially he devoted his personal efforts to a systematic study of the substituted amines in whose discovery he shares equally with Charles Adolph Wurtz. Meanwhile he assigned his students to related inquiries (*9*). To Charles Mansfield he assigned the fractional distillation of light coal oil. This research yielded an inexpensive industrial method of obtaining benzene and toluene of high purity. Unfortunately Mansfield's promising career ended in tragedy a few years later when a large still broke and caught fire, burning him fatally (*10*).

More frequently, the kind of project to which Hofmann assigned his students was the nitration of some aromatic hydrocarbon and its subsequent reduction to an amine. To young William H. Perkin, for example, he gave the task of making the amine of anthracene and later, when the lad failed in this assignment, he told him to try the reduction of dinitronaphthalene (*11*). Likewise, to Edward C. Nicholson, Frederick Field, and Frederick Abel, Hofmann suggested the amination of cumene and pseudocumene and the study of the chemical properties of the products of these experiments. Occasionally he would also put one of his assistants to work on the analysis of an alkaloid such as caffeine, morphine, and quinine. Since not much was then known about the theory of organic structure, Hofmann speculated that his aromatic amines might be the building blocks for these much-sought-after drugs. He proved to be utterly wrong, but it was in the process of looking for a synthesis of quinine from aniline that Perkin stumbled onto mauve and ushered in the era of synthetic dyes (*12*).

"Cradle of the Aniline Dye Industry"

It is principally as the cradle of the aniline dye industry that the Royal College is best remembered, and this is as it should be. With historical hindsight it is now evident that the researches carried out there before Perkin's synthesis of mauve in 1856 unknowingly prepared the way for the rapid discovery and subsequent manufacture of more new coal tar colors. Once dye production had begun, it was to Hofmann at the Royal College that dye factory owners quite naturally turned when faced with problems that required the systematic approach of an expert. Several of these pioneers in aniline color manufacture were graduates of, or had once assisted in, the laboratories of the Royal College. Time and again they supplied Hofmann with intermediates and new dyes whose composition was unknown, and seldom did he fail to come up with the answer. In fact, it was he who first brought order out of the bewildering variety of colors that were discovered in rapid succession in those early years of wild experimentation when fortune hunters eager for gain subjected the wonder-base aniline and related compounds to any oxidizing agent they could find. Hofmann, his assistants, and students were able to show that most of these colors, such as aniline yellow, blue, and purple, were all structurally related to aniline red which was then sold under the trade name Fuchsin, and which Hofmann renamed rosaniline. He assigned rosaniline the formula $C_{20}H_{19}N_3$, and later determined that it was composed of one mole of aniline and two moles of toluidine (*13*). Beyond that, however, he could not probe, it remaining for Emil and Otto Fischer fourteen years later to determine the structural formula of this and the related triphenylmethane dyes (*14*).

With this work on rosaniline-type compounds, which Hofmann called "polyammonias," we come to the end of his research activity in London. Why he left that city which after twenty years he had come to love so well and where he had been repeatedly and highly honored, became the object of much discussion around the First World War when it was noticed that Britain's now dangerous lag behind Germany's chemical industry began just at about the time of Hofmann's departure in 1865. Some said Hofmann's resignation had caused the decline. The more astute pointed out that it was more a symptom of the decline. British chemical industry and the government, they pointed out, had failed to take full advantage of Hofmann's abilities. The failure of the Royal College of Chemistry to grow and prosper proved that Victorian Britons had really not been in earnest about their desire to see chemical instruction raised to the university level as Leibig had done.

We may assign three reasons for this mid-century indifference to the fate of England's fine chemical industry and chemical education. First, it was felt that since mechanics, foremen, and vocationally-trained technicians had masterminded Britain's commanding industrial lead in the first half of the nineteenth century, the same could be relied upon to maintain this lead in the future. Second, there was a widespread prejudice in aristocratic and academic circles against university graduates who stooped to working in factories forsaking the quest for pure truth for the pursuit of material gain. Third, England could temporarily afford to neglect her organic chemical industry (*15*). Her unmatched level of prosperity resting as it did on such a broad economic base, made the loss of leadership in one or two areas appear inconsequential. Not until the specter of rising German industrial and military power frightened Britons into an "agonizing reappraisal" of their science and technology did Englishmen move decisively to reclaim the heritage bequeathed them by A. W. Hofmann and the Royal College of Chemistry.

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Introductory Courses in Physical Chemistry for Non-Majors

The groups of non-major students for whom physical chemistry courses are designed are those interested in the biological sciences and those who are preparing for engineering. A group which has been small in number, but is now of growing importance, includes those who are preparing for science teaching in the secondary school or who are undergoing some sort of teacher in-service refresher program.

A consideration that leads to differentiation of content from that in the usual course is lack of time in the curriculum. At the University of Florida, the physical chemistry course for majors has been for some years past a three-semester sequence. This makes the factor of time to devote to chemistry on the part of non-majors more critical, for many of the ideas of considerable importance to them, such as those of molecular structure and valence, have been included in the third semester. Even more significant as a cause for differentiation, particularly for those who are biologically inclined, is a deficiency in mathematical background, which usually does not include calculus.

In the following part of this paper, there will be discussed some of the techniques which have been developed, and some of the considerations which have appeared important to the writer, in teaching a one-semester course, primarily for "biologists," in three different institutions over the past ten years (*1*). The limits imposed by time require that careful selection of subject matter be made. One means of achieving greatest efficiency is the introduction of a few basic, comprehensive principles, which are then repeatedly applied and illustrated. Many of the applications, it is true, may be encountered in other courses such as biochemistry; the aim of the physical chemist should be to show how the fundamental principles tie them together.

Those interested in biological sciences include premedical students together with graduate students in biology, biochemistry, microbiology, physiology, agriculture, soils, sanitary engineering, pharmacy, and related areas. On the one hand, the pre-meds usually have insufficient maturity to appreciate at the start the usefulness of physical chemistry, but generally they have just been through quantitative analysis and college mathematics of some sort and are thus reasonably well prepared. The graduate students, on the other hand, present different problems. They are usually well-motivated, for they have in view some problem which requires a physico-chemical background, but they are often years away from elementary chemistry.

The selection of subject matter, obviously, will vary with the particular group of students. For example, those adequately prepared will require little emphasis on elementary chemistry of ionic solutions, acid-base effects, indicators, and many other matters usually taught in quantitative analysis. It is then possible to develop more advanced concepts of solution theory, such as ion-ion and ion-solvent interactions, the salting-out effect, ion strength effects, electrolyte activities, and factors affecting mobility of ions, with obvious later applications to proteins, biological fluids, and other colloidal systems.

Electrolyte Solutions

Unfortunately, in the writer's experience, few people arrive in the physical chemistry course with mastery of the fundamentals of electrolyte solutions, and it is necessary to devote extended time to coverage of this material. In presenting the elements of acid-base effects, the generalized concept of Brønsted, employing in calculations chiefly the pK_a value of the acid member of a conjugate pair, conveniently replaces a multiplic-

Presented as part of the Symposium on Instruction in Physical Chemistry before the Division of Chemical Education at the 136th Meeting of the American Chemical Society, Atlantic City, September, 1959.

ity of types of hydrolysis constants and particularized equilibria (*2*). Emphasis then follows on the familiar equation

$$pH = pK_a + \log \frac{[\text{Base}]}{[\text{Acid}]}$$

with its applications to common ion effects, indicators, titrations, and buffers. It should be mentioned that much of the biological literature on acid-base balance uses the terms acid and base as synonymous with anion and cation, respectively, and students will be confused by this if not warned about it.

The situation with respect to level of treatment of oxidation-reduction reactions parallels that of acid-base effects. It is helpful in an elementary presentation to draw an analogy between the Nernst equation and the equation for *p*H in an acid-base pair: the first term of each is a constant characteristic of the intrinsic electron or proton availability of a particular couple, the second is a term varying with the ratio of concentration of components of the couple, and either equation is applicable only when both components of the couple are present in measurable quantities. In the discussion of redox reactions in biochemical systems, the difference between equilibrium considerations and kinetic considerations is stressed, as exemplified by the participation of a potential mediator or enzyme catalyst in an actual process. Again a problem of terminology must be pointed out: biochemical redox potentials are usually quoted with signs reversed from those in the physical chemistry convention. Apology need not be made for this circumstance, provided the neophyte has been warned.

Fundamental Thermodynamics

Students appreciate more fully both proton-transfer and electron-transfer equilibria, and especially the Nernst equation, if these are presented as based on a thermodynamic foundation. A treatment of thermodynamics on an introductory level has therefore been introduced near the beginning of the course; this is given quite adequately at the required level without use of calculus. A few equations must be stated without derivation, but these can at least be made plausible; this procedure is not contrary to the spirit of empirically founded thermodynamics. For example, in discussing the vapor pressure of a liquid, the proportionality of negative logarithm of vapor pressure to reciprocal of temperature and the relation of the heat of vaporization to the constant of proportionality are presented as experimental facts. The definite integral form of the vapor pressure-temperature equation is then derived by application to two different temperatures. To justify the van't Hoff equation, it is pointed out that the liquid-vapor equilibrium is a special case of the more general category of equilibria, and the integrated form of this equation then appears reasonable. Later, the Arrhenius equation for rate constant dependence on temperature is shown to be another special case (*3*).

The principal tool uses of thermodynamics are related to enthalpies of reaction (thermochemistry), of which there has been relatively long-standing application to the energetics of biological processes, and the correlation and prediction of equilibria by the use of the free energy. The basic qualitative ideas of free energy as a measure of potential force driving to attainment of equilibrium and of entropy as a measure of disorder are presented. The relation of energy available for doing work to chemical equilibrium is strikingly shown in the derivation of the Nernst equation. Biochemists refer to the presence of a "high-energy phosphate bond" in a compound; what is meant is a bond that is broken in a hydrolysis process with which is associated a large negative free energy change (*4*).

Heterogenous equilibria are treated in some detail. The basic similarity of equilibrium considerations here to those in other cases is emphasized. Phase diagrams are presented as compact descriptive summaries of experimental results. Colligative properties of solutions, including osmotic pressure, are treated in terms of vapor pressure, or relative escaping tendency, as a driving force for interphase transfer. For biological applications, the emphasis in osmosis is on differential permeability and tone, or effect with respect to an actual membrane, rather than with respect to the ideal membrane, permeable only to the solvent. A number of techniques of importance in biochemical laboratories are shown to be applications of differential rates of transfer between phases: liquid-phase column and paper chromatography, gas-phase chromatography, distillation, and liquid-liquid extraction.

Mechanism and Rate of Reaction

In the area of chemical kinetics, the rate of a process is carefully defined, and the basic ideas of the derivative and the integral are presented so that they can be comprehended by students who have not previously encountered them. It seems essential to emphasize the complexities of actual reactions, including reversible, consecutive, and catalyzed reactions. Learning the mere technique of fitting data to integral order equations is not so productive as understanding the general relations between rate, mechanism, and concentration. The hypothesis of the stationary state and its limitations are clearly stated, with applications to simple cases of acid-base catalysis and to enzyme-catalyzed reactions. The "energy-barrier" picture of rate processes is described, and the nature of information obtained from measurement of the temperature coefficient of rate constant is discussed. The reaction of protein denaturation is an example affording a contrast between enthalpy of activation and free energy of activation; the reaction occurs at a reasonable rate at room temperature, although the enthalpy of activation is large, because there is also a large positive entropy of activation.

Colloidal Systems

Colloids are treated as complex systems in which particular features of structure on a scale intermediate between the micro- and macro-scales contribute appreciably to the properties of the system, but which are governed by the same rules of intermolecular forces and thermodynamics as are simpler systems. The importance of colloids is evident upon examination of any text in biochemistry; in that by Gortner and Gortner (*5*), the first quarter is devoted to colloids. The function of the physical chemistry teacher is to supply the

basic principles which afford a means of correlating the vast amount of descriptive material concerning colloidal systems. As an instance may be cited the treatment of adsorption in terms of surface free energy. Here, too, free energy and enthalpy are to be distinguished. The physical considerations involved in such biochemical techniques as electrophoresis and ultracentrifugation are described.

Structural Concepts

The molecular structure viewpoint, with its consideration of molecules as three-dimensional entities, is one of the most important areas on which emphasis can be laid. The growing importance of structural chemistry and stereochemistry in the elucidation of biochemical function has made the development of the ability to think in structural terms mandatory for the biologist. The first level of approach is that of three-dimensional geometry, of the sort needed to comprehend, for instance, the protein helix picture or the structure of nucleic acids. Enzymologists have employed lock and key diagrams to illustrate specificity schematically; these are now in process of being translated into chemical-geometrical equivalents. Intramolecular flexibility or stiffness and ease of changing conformation are discussed.

A second level of approach to structure is that of "valence bond theory," of course on a very elementary level. The wave nature of the electron, orbital hybridization, and resonance, presented as an approximation required because the chemist cannot account for observations of molecular behavior by employing single structures with an integral number of electron pairs, are treated. Both as a basis for describing electron behavior in relation to valence and as a foundation for description of experimental techniques for determining molecular structure, the nature of electromagnetic radiation is discussed, including diffraction and refraction effects. An elementary discussion of molecular spectroscopy and its use as a tool follows. The nature of metal ion complexes and the atomic orbital basis for their formation is described.

For the instructor who wishes to broaden his background in biological applications of chemistry and physics, there can be recommended books by Bull (*6*), Clark (*7*), West (*4*), Jirgensons (*8*), and Edsall and Wyman (*9*). The last gives an intensive treatment, at a fairly advanced mathematical level, of many pertinent subjects.

Basic Physical Chemistry for Engineers

Let us now turn to the other group of prospective students—those who are preparing for careers in engineering. Recently a number of engineering colleges have introduced as a general requirement a semester of chemistry beyond the freshman course. The choice for this purpose seems logically to fall upon an introduction to physical chemistry. The combination of thermodynamic and structural viewpoints is a convenient foundation on which to build a course that gives insight into properties of materials, corrosion processes, the relation of electricity and chemical change, and so on. Covalent bonding, with an introduction to organic chemistry, the chemist's approach to thermodynamics, the nature of solid structure and the energy relations in various sorts of solids, the distinctions between equilibrium limitations and kinetic limitations, the interactions of radiation with matter, and surface effects would all seem to deserve fairly detailed treatment in such a course.

In teaching any group where motivation is a problem, it is important to use, as illustrations of the principles being developed, examples relating to the particular field of interest of the group. Generally this can be done without inclining the approach too much in the direction of applied or descriptive material. In addition, the teacher in a course for non-majors is concerned not so much with rigorous derivations from first principles as in conveying appropriate meaning and significance to the important relationships and equations. For the user of physical chemistry, the approach can be different from that for the professional chemist, who will later be expected to contribute new developments. For the user, the justification of any equation is its empirical success. However, derivations and presentation of theoretical foundations are pedagogically justified to the extent that they provide a framework into which the learner fits details of knowledge.

Finally, the strong temptation to present the subject matter of physical chemistry as a finished structure, in order to compress material into a limited period, should be resisted. The teacher can endeavor to convey, both in substance and in spirit, the added interest and challenge associated with an actively expanding area on the scientific frontier.

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Graduate Examination Practices at the M.S. and M.A. Levels

It appears to be quite common practice to subject entering graduate students in chemistry to a series of comprehensive examinations. These tests may be administered for diagnostic purposes, orientation in subsequent programs, evaluation of comprehension in the several basic branches of chemistry, or for possible elimination of the candidate from further graduate study. Regardless of the purpose, nature, extent, and application of these examinations, it is quite obvious to even a casual observer that practices vary greatly from department to department.

Literally dozens, if not hundreds, of studies have been made and reported on test construction and use. Many of these findings are of real value in related areas of teaching. The development of the Cooperative Chemistry Tests (*1*) as a part of a cooperative endeavor of the Committee on Examinations and Tests of the Division of Chemical Education and the American Council on Education through the Cooperative Test Service, was a significant movement. While College Entrance Examinations (*2*) have served quite a different purpose, they have again emphasized the importance of careful entrance screening. The Division of Chemical Education held a Symposium on Tests and Examinations (*3*) at the ninety-first meeting of the ACS in Kansas City, Missouri, on April 14, 1936. A number of college tests have been devised from time to time for diagnostic purposes (*4*, *5*). Frost and Hussey (*6*) have recently reported the results of three years' experience with cumulative examinations for the Ph.D. degree at Northwestern University. The results appear to be encouraging and worthy of more consideration. Undoubtedly the techniques could easily be applied to other areas of graduate study.

However, an extensive study of the available chemical literature produced little if any information regarding current or best practices for administering graduate entrance examinations in chemistry. It was for these reasons that a brief questionnaire was prepared, regarding such procedures at the M.S. and M.A. level, and mailed to the chairman of each chemistry department on the "List of ACS Approved Schools" (*7*). A total of 250 such questionnaires was mailed. The unusual interest in the subject is indicated by the fact that 211 or 84.4 % of the schools responded with completed replies. A tabulation of these schools indicated that 98 were state tax-supported institutions, 72 were privately- and municipally-operated schools, and 41 were under denominational control. It was also encouraging to note that in most instances the information requested was supplied by the chairman of the department or someone closely associated who was equally qualified to supply the desired information. Likewise, over 25% of the respondents requested a tabulation of the total findings.

The original questionnaire included ten basic questions with several subtitles thereto. The results were tabulated and can best be stated and discussed in turn. Of the 211 replies, it was found that 165 schools offer either or both the M.S. and M.A. degrees in chemistry. A total of 46 offer no graduate work at all, or not, at least, in the field under investigation. Future considerations will, therefore, be confined predominately to those 165 institutions offering graduate work in chemistry. It was discovered that 111 departments offer a series of comprehensive orientation or qualifying examinations to all entering graduate students in chemistry. The remaining 54 schools deviate somewhat in practice. Some give special consideration to their own undergraduates or graduates of ACS accredited departments. Others critically evaluate the transcripts of applicants and base their testing programs on apparent deficiencies. It was discovered that several require such tests only of potential Ph.D. candidates but not at the M.S. level. Others have varied the practice from year to year and are apparently still seeking a logical and effective technique. However, it is interesting to note that of the 111 requiring entrance examinations, 90 (81.1%) test entering graduate students in all of the four traditional areas of chemistry, namely inorganic, analytical, organic, and physical. The remaining 21 schools deviate, often by requiring three of the four areas or the substitution of another subject such as biochemistry for some other branch, depending upon the future plans of the potential graduate student, the use of the ACS Cooperative Tests was not as extensive as was anticipated, for only 46 departments apparently relied on their use periodically or exclusively. The Graduate Record Examinations (*8*) were preferred by many. But the vast majority (69.4%) prepared and administered their own examinations, within the department.

It appears to be standard practice, where such examinations are required, to administer the same at an early date in the graduate training program. A total of 94 (84.8%) of the schools, require these examinations upon entrance, the remaining 17 at a later date, frequently quarter by quarter, semester by semester, or on demand. Some even permit the candidates to select the opportune time for such testing. Perhaps the greatest deviation was found in the limitations, if any, that were placed on the number of times that these examinations could be repeated. In at least 10 instances no repeat trials were permitted. We may, therefore, assume that any failure in these examinations would ordinarily result in the automatic elimination of

the candidate. However, it must be noted that these same schools may require only a portion of the tests or passage in a fraction of the examinations taken. Likewise, the results of these examinations are frequently used only for diagnostic purposes, rather than student suspension. It was found that 34 departments permitted one repeat trial for each portion of the examinations. This was the most common practice. Two repeats each were permitted by 22 schools; three repeats by 7; and four repeats by 1. While it may appear that the remaining 37 schools have no restrictions on the number of times these examinations may be repeated, in reality most of them place very rigid limitations, for in most instances no research work is permitted until the entire battery of examinations is satisfactorily completed.

A final comprehensive examination in the major field is required in 110 instances, as compared to the 111 schools that administer entrance examinations. A total of 41 schools require no such examination. The remaining 14 schools vary the practice, depending on the student, nature of the program, desire of the advisor, and other factors. Where such a final examination is required, 37 use the oral approach exclusively, 21 the written, and the remaining 52 a combination of the two as the immediate conditions warrant. Of the 165 departments offering the M.S. or M.A. degree in chemistry, 104 definitely require a thesis based on research experience and findings. However, 21 require no such thesis, while the remaining 40 follow a variable practice, apparently depending on the program, background, and future plans of the student, and other pertinent factors. It appears to be a far more common practice to require a final oral examination in defense of the thesis; 121 schools follow this practice, 31 do not require such a defense examination, and the remaining 13 departments vary the practice from program to program, and one major field to another.

Descriptions of a number of additional observations and practices were appended to questionnaire answers. One school does not give any entrance examinations but substitutes a series of four basic graduate courses required of all graduate students. Subsequent programming and decisions regarding the graduate student depend upon his performance in these courses. The program apparently is working well, and students feel they are getting a "square deal." Many departments have more rigorous entrance requirements for the Ph.D. than M.S. degree. A prominent mid-western institution gives four comprehensive examinations at the end of the first year of residence. Failures may be repeated once. A large eastern school uses the results primarily to determine which undergraduate courses should be repeated. Another states that the placement examination is used only for guidance. Many institutions treat M.S. and Ph.D. candidates alike, insofar as entrance requirements are concerned. Others admit candidates for the Ph.D. degree only, but later award an M.S. degree for questionable students. A few schools place less emphasis on the preliminary examinations, and proportionally more on the final tests. However, the converse is more often true. One department substitutes at times a comprehensive library research paper in lieu of the usual entrance examinations. Several instances were found of permissible substitutions such as mathematics, physics, biochemistry, or others, for the traditional four branches of chemistry in these examinations. Frequently the defense of the thesis and the major examination are combined. The final examination is often a presentation of research findings open to all graduate students as a seminar. The oral examination in defense of the thesis frequently covers both thesis and course work. A rather unique arrangement was found wherein a series of comprehensive examinations were given in turn at the end of each semester over a two-year period in analytical, inorganic, organic, physical, history of chemistry, and German after corresponding graduate courses were completed in each area. One comment indicates that no examination is given to all entering students, but each candidate appears before a committee at which time an appraisal of outstanding weaknesses and research interests is obtained. Some institutions administer qualifying examinations, after apparent undergraduate deficiencies have been corrected by enrollment in corresponding review courses.

In addition to the factors and conclusions which are immediately obvious from the tabulations above, the following generalizations seem to emerge as a result of this study:

(1) Entrance or qualifying examinations are standard practice for admission to graduate study in chemistry at most ACS accredited institutions.

(2) These examinations are most often administered before enrollment, or at least very early in the period of graduate study.

(3) These examinations most frequently cover the areas of inorganic, analytical, organic, and physical chemistry. Occasionally a slight choice in the above list is permitted. More frequently additions or substitutions are made, and these most often include physics, mathematics, German, biochemistry, or some other branch of related chemistry.

(4) While ACS Cooperative Tests are frequently used, their adoption is not as extensive as might be anticipated or desired. Examinations prepared by the staff, within the department, are preferred. The Graduate Record Examinations appear to be gaining in popularity.

(5) Increased care in enrolling potential graduate students appears to be exercised. The examinations are then used more extensively for diagnostic purposes and remedial instruction, rather than student elimination. Under this philosophy there is less need to repeat these examinations, and student programs are adjusted early according to their undergraduate deficiencies.

(6) Increased emphasis is being placed on undergraduate training and transcripts. An over-all average of "B," and particularly in basic courses, is nearly a "must" for graduate admission. The classification of an undergraduate department as "ACS Approved," is significantly important in obtaining admission consideration for their undergraduates to other graduate schools in chemistry. Increased consideration is being given the quantity and quality of instruction also in mathematics, physics, German, and related subjects, as well as chemistry.

(7) A final comprehensive examination in the major field of study is usually required. The oral and written

approaches are both extensively used. In addition a final oral examination in defense of the thesis is commonly required. This may be combined with the former major examination in a more comprehensive test.

(8) While the no-thesis or non-research option is occasionally permitted, it is the rare exception. Early participation on the part of the entering graduate student in seminars and other graduate activities is encouraged. Likewise the evaluation of early research interest is essential, and the same should be encouraged and supervised by competent staff members.

(9) Outstanding undergraduate scholastic performance is frequently rewarded by exemption from corresponding graduate entrance examination requirements.

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Closed-Circuit Television as a Supplement to the General Chemistry Program

During the academic year 1958–59 closed circuit television was employed in the general chemistry course at Case as a means of augmenting the program, not as a method of displacing live instruction.[1] Supplementation and not replacement was the basic premise; this application of television required an increased teaching staff.

Television was utilized in the lectures to show apparatus which was permanently mounted in research laboratories and enlarged views of experiments on the lecture table which involved equipment too small to be seen by the whole class.[2] It was also used in the laboratory in connection with an experiment on the mass spectrometer.

Students viewing a telecast of the mass spectrometer

In those lectures which were supplemented by television short periods of live instruction were interspersed with televised demonstrations, a procedure which called for rehearsals and careful synchronization. This was made possible by means of two-way sound and an independently manned two-way telephone. In addition it was found that smooth presentation required separate personnel for the television camera, the monitor, the slide projector, and the lights and continuity sheet. The following paragraphs outline the manner in which television was used in specific instances.

Research Instruments. This demonstration was used to present the methods of operation of certain instruments, the types of results that they yield, and the means used to convert these results into the solution of research problems. The central theme of the lecture was the nature of MgO. In the course of the hour the students were shown a televised view of MgO through a light microscope, a televised view of an electron microscope in operation, a slide of MgO as viewed with an electron microscope, a televised view of a powder X-ray diffraction unit, and a slide of a typical film from it. A short lecture was given for each of the instruments and it was shown that the information obtained from these instruments together with additional information and calculations could be used to obtain a very accurate description of MgO in terms of its atomic arrangement.

After this sequence it was pointed out that the atomic structure of certain materials can be approached best by other techniques. To illustrate this point the operation of a recording infrared spectrophotometer with a sample of ethyl alcohol was televised.

Titration Curves. In connection with the lectures on ionic equilibria a televised experiment on titration

[1] The program was supported by a grant from the Case Project.

[2] Additional information on this type of demonstration is given by GLEMSER, O., J. CHEM. EDUC., **35,** 573 (1958).

curves was set up. It differed from the others in that it was performed in front of the class and closed circuit television was used to furnish each student with an intimate view of the results.[2] During the experiment the students were given televised views of the buret-*p*H electrode assembly and of the chart recorder connected to the *p*H electrodes. It was shown that points picked off the curves (NaOH-HCl, NaOH-HOAc, and NaOH-H_3PO_4) were in agreement with those calculated according to theory.

Polymers. Because of the availability of the polymer laboratory at Case, it was possible to let the students see televised views of some of the equipment used for polymer fabrication and to give them some feeling for chemistry as applied on an industrial scale. The lecture was built around the chemistry involved in the conversion of coal, water, limestone, and salt into finished polyvinyl chloride objects. During the lecture the students saw shots of a roller mill compounding raw P.V.C. resin and of an injection molding machine making milled P.V.C. into finished objects. The operation of a vacuum former was also televised.

Mass Spectrometer. This was the only attempt at using closed-circuit television in the laboratory and was based on the idea that more interesting and informative freshman experiments could be developed by making a wider range of equipment available for use. The mass spectrometer was chosen as the subject of the demonstration because it is an instrument that gives information which is meaningful to freshman and yet one that is ordinarily out of reach. In the experiment the students were given views of the instrument while the mass spectra of methane, a chlorinated hydrocarbon, and a mixture of the two were being obtained. The data that the students thus gathered, together with additional information, enabled them to identify the major peaks of the spectra and to calculate the isotopic ratio for chlorine and the composition of the mixture.

Closed-circuit television made it possible for the freshmen to see in action instruments and equipment that under ordinary circumstances must be reserved for the use of upper classmen. This stimulated interest in chemistry and enlarged the scope of the freshman program; as a result it is felt that the project was a success. In general, the students seemed to respond favorably to television under the conditions of this project. It should be reported, however, that the total cost of the program was too high to allow for the wholesale use of this type of lecture demonstration. Inasmuch as television equipment was readily available on campus the major portion of the expense was in the preparation required by the experiments chosen for use.

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Laboratory by Discussion

Courses where laboratory manuals are used are commonly described by students as "cookbook chemistry." Manuals are used as crutches by both students and teachers. Their instructional value is confined to having the students answer "thought-provoking" questions, and—unfortunately— these answers are often copied. Quite often the performance of an experiment does not provide enough information to reveal its purpose or to answer questions. At best, a manual serves as a handy reference for experimental procedures and materials. No matter how ingeniously designed, it limits the possibilities of a laboratory course.

Many teachers have run so-called "problem laboratories" or operated without a laboratory manual for some experiments. The author has extended this technique to the entire course and relies solely on class discussions to prepare his students for laboratory work. General chemistry classes of 10, 35, and even 100 students and physical chemistry classes of 20 students have responded well to this procedure.

The first meeting of the class is devoted to outlining the discussion method. Students are told that experiments will not be announced in advance, that their laboratory work will depend entirely on the notes they take during discussion, and that no collaboration will be permitted. Those who have previously performed the experiment or read up on it are requested not to participate in the discussion. If the experiment requires preparatory work (as is the case in physical chemistry), the discussion is held a few days before the laboratory period.

Report writing is also taken up at the first meeting. After this initial discussion of reports, the students are left to their own devices and are graded partially on the organization and completeness of their notebooks. These are collected at the end of each laboratory period and returned graded the following period.

No difficulty was encountered in having the students follow these rules.

The discussions, which last about thirty minutes, can be facilitated by grouping the students in the front seats of a lecture hall or around a blackboard in the laboratory. The problem is first presented in general terms. For instance: instead of asking, "How is a molecular weight determined by the gas density method?" the question is "How would you determine the molecular weight of a substance?" If there is no response to this opening question, it is usually good prac-

tice to let the students mul lit over for a few minutes. Struggling with an experimental problem gives them an appreciation of the difficulties involved in the design and execution of an experiment. After a few minutes of no response the teacher can ask some leading questions or supply hints.

The teacher has to lead and direct the discussion in such a way that the class is led "spontaneously" to reach conclusions predetermined by the teacher. The students' suggestions are listed on the blackboard, and they are then told which ones will be followed. They are asked what quantities will have to be determined and with what accuracy. Once these quantities are known the discussion shifts to experimental procedure— "What do you measure? In what order? How?"

Next the class is asked to design an apparatus and to suggest a chemical system for testing. All suggestions, unless patently ridiculous, are discussed as to their merits.

Since the laboratory is stocked with equipment and reagents for predetermined experiments, the students are told at the end of the discussion what apparatus is available, the exact quantities of reagents to be used, the results to be reported, and other special instructions.

The steps in this method may be summarized as follows:

(1) Present the problem in general terms
(2) Present the specific problem
(3) Find out what quantities and qualities must be determined
(4) Set up an experimental procedure
(5) Choose a practical chemical system
(6) Design the experimental apparatus
(7) Point out the available equipment, reagents to be used, and the results to be reported

One drawback to the lab-by-discussion method is the teacher who is unwilling to take the time to prepare for, organize, and lead a group discussion. Most teaching techniques read well on paper, but they have to be implemented by interested and effective teachers. Leading a group discussion is an art, and it takes some time to become skillful in it. However, it is the author's opinion that the lab-by-discussion method is inherently better than relying on laboratory manuals.

First and foremost, the student can perform the experiment only if he listens and takes notes. Secondly, the discussion gives students the feeling of participation in the design of the experiment. The degree of this feeling depends on the size of the class and the skill of the teacher as a discussion leader. It is wise to *actually* let the students design the experiments (keeping in mind the available equipment and reagents). This flexibility serves a secondary purpose of keeping teacher interest alive by continually varying the experiments.

The method can be applied to experiments in any undergraduate chemistry course. Where the procedures are complex, the problem is merely to supply more information to the students at the end of the discussion. The size of the class only restricts the extent of student participation.

The lab-by-discussion method is an attempt to give the student a feeling for and an appreciation of the art of laboratory experimentation. It is an attempt to teach how to carry out an experiment from beginning to end rather than how to copy and answer tricky questions.

A questionnaire designed to test student opinion on the lab-by-discussion method showed that all of the groups tested favored this method by about three to one over methods using laboratory manuals. Students were also overwhelmingly in favor of having some discussion on the experiments before performing them. One of the students commented, "The method used now makes one feel that he and his fellow students are doing the experiment, *in toto*, rather than being assistants to the author of the lab manual."

Improved Value for the Faraday

A new electrochemical determination of the faraday has been accomplished at the National Bureau of Standards. This physical constant, named in honor of Michael Faraday, is the quantity of electricity associated with a change of one equivalent weight of the reacting substance in any electrolytic process. The recent electrochemical work was carried out by D. N. Craig and W. J. Hamer, with the assistance of Catherine Law and J. I. Hoffman. In essence, they determined the electrochemical equivalent of silver by measuring the mass *dissolved* by one coulomb of electricity. This together with the atomic weight of the silver used in the experiments gives the new value of the faraday.

Preliminary values indicate that the faraday is 96,516.4 ± 2.0 coulombs per g equivalent on the physical scale or 96,489.9 ± 2.0 coulombs per g equivalent on the chemical scale (using 1.000275 as the conversion factor).

Efforts during the past 100 years to obtain an accurate value for the faraday have not been very successful. For over 40 years a discrepancy has existed between the values yielded by the two most precise electrochemical methods—the silver coulometer and the iodine coulometer.

As the faraday depends upon the equivalent weight, or in this case atomic weight, of the material involved in the electrochemical change, the atomic weight of the silver used was determined in an associated experiment. This evaluation was carried out by V. H. Dibeler and W. R. Shields with a mass spectrometer. The value for the atomic weight of silver derived from this work is 107.8730 ± 0.0015 (chemical scale) representing a 95 per cent confidence interval.

In the Bureau's recent determinations, purified silver was used as an anode and dissolved in a solution of perchloric acid by an electric current. The silver was weighed at the beginning of the process and again after an accurately measured quantity of electricity had passed through a coulometric circuit. This corrosion process can be carried out so accurately that it can be employed as a rapid and reliable method for checking on the stability of electrical standards.

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Fluidization as an Undergraduate Unit Operation Experiment

Many unit operations laboratory experiments are often complex and more or less fixed in their scope by the nature of the equipment used. It has been suggested that experiments be developed which would be inexpensive, flexible, and of course, uniquely characteristic of chemical engineering alone (*4–7*). One such experiment would be on the subject of fluidization which is one of the newer fields in chemical engineering (*1, 2, 8*). An experiment of this nature is described below.

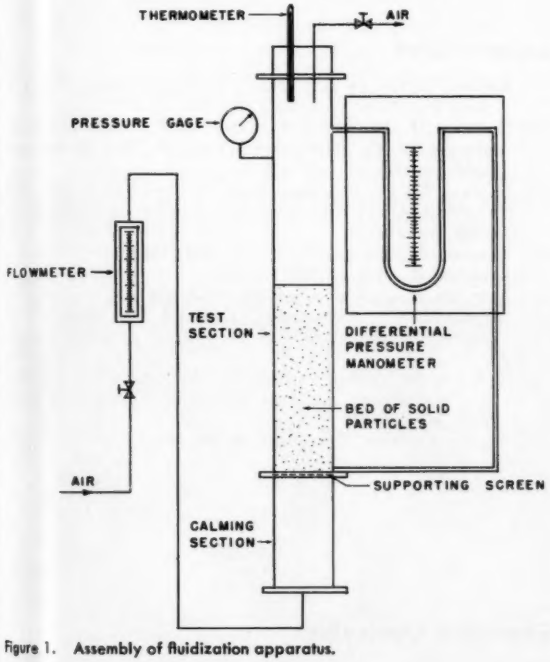

Figure 1. Assembly of fluidization apparatus.

A sketch and flow diagram of the apparatus is shown in Figure 1. The test section, one inch in diameter, may be constructed of iron pipe or preferably of glass pipe for visual observation.

The Experiment

1. A measured quantity of solid particles is placed in the column.
2. Completely fluidize the particles and then allow to resettle in order to obtain reproducible porosity.
3. After the packed bed is formed following the preliminary fluidization, the upward flow of air is resumed with gradual increase of its rate. The pressure drop across the bed increases with the increases in the air flow rate until the frictional drag on the particles becomes equal to their effective weight (actual weight less buoyancy). This point is called onset point of fluidization and further increase of the air flow rate beyond this point causes the individual particles to separate from one another and become freely supported in the fluid. This implies that the "fluidization" commences by increase of fluid flow rate beyond the onset point. The use of glass pipe enables the students to make visual observation of this onset point.
4. After the onset point is reached, the flow rate of the air is increased further until the point where particles begin to escape from the test section. The flow rate of air corresponding to this point is called maximum fluidization velocity.

The pressure and temperature in the test section are maintained constant during the experimentation, and the air flow rate and corresponding pressure drop are recorded. The students are also asked to record any visual observation they may make during the experimental runs. Channeling, slugging, fluidization onset, bed expansion, and elutriation of the particles from the column are the typical phenomena they may observe.

Figure 2 illustrates a typical set of data. The line drawn represents the calculated pressure drop. For

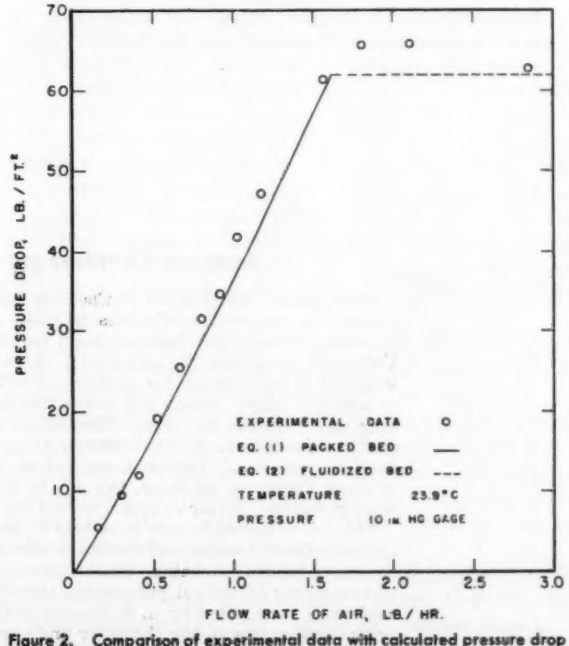

Figure 2. Comparison of experimental data with calculated pressure drop for 0.07 cm spheres. (True density of spheres—2.5 g/cm³. Bulk density of spheres—1.5 g/cm³.)

the pressure drop through the packed bed before the fluidization, Ergun's equation (*9*)

$$\frac{\Delta P}{L} g_c = 150 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu U_m}{D^2_p} + 1.75 \frac{(1-\epsilon)}{\epsilon^3} \frac{G U_m}{D^2_p} \qquad (1)$$

was employed. Other equations are available in the unit operation textbooks (*1, 2, 3, 8*). Since the pressure drop across the fluidized beds is equal to their effective weight, it can be estimated as:

$$\Delta P = \frac{W}{A} \left(\frac{\rho_s - \rho_f}{\rho_s} \right) \qquad (2)$$

The air flow rate which corresponds to the visually observed onset point should be compared with the onset velocity estimated from the pressure drop versus fluid flow rate curve as indicated in Figure 2.

Modifications

The basic scheme of this experiment outlined above may be modified or enlarged to cover other aspects of fluidization and other related phenomena of the solid particle-fluid contact operations.

The various materials, other than spherical glass beads used in this experiment, are available as solid particles. The use of various shapes and sizes of the particles enables students to demonstrate and observe their effects on the smoothness or quality of the fluidization. The different weights of the same particles may be charged in the test section to demonstrate the fact that the onset velocity is independent of the total weight of the bed. The air used as a fluidizing medium can easily be replaced with water or other liquids to create an entirely different mode of fluidization. With a liquid as a fluidizing medium, the solid particle beds continue to expand as the velocity of liquid is increased, and these solid particle beds will maintain their uniformity. With a gas, however, except at relatively low velocities, two separate phases are formed within the beds and the pressure drop across the bed will fluctuate considerably. The former mode of fluidization is called "particulate fluidization" and the latter "aggregative fluidization."

The use of two different sizes of the particles will allow the students to measure the rate of elutriation and to correlate it in the form of the first order rate equation as suggested by Leva (*2*).

In addition to the estimations of pressure drop and the onset velocity, the comparison of the falling rate of the particle with the maximum fluidization velocity and the correlation of bed expansion with respect to the operating conditions can also be carried out. If budget allows, the columns of other sizes may be used to show, at least qualitatively, the effect of column size on the behavior of the fluidized beds.

As can be seen from the above description, this experiment can illustrate not only the principles of fluidization, but also the fluid dynamics of fluid flowing through a packed bed and other related principles of solid particles-fluid contact operations. In other words, we may count the flexibility and extensiveness of its scope as well as the relatively low cost and simplicity of the apparatus employed as advantages of this experiment.

The author wishes to thank Dr. Henry T. Ward, Head, Department of Chemical Engineering at Kansas State University, for his encouragement and advice in setting up this project.

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Summer Conferences on Chemistry Curriculum

This summer the Division of Chemical Education of the ACS, supported by the NSF, will sponsor two one-week conferences on topics concerning chemistry at the undergraduate level. The first of these, "The Undergraduate Training of Chemistry Majors," will be held at Bucknell University, Lewisburg, Pa., June 12–18. This conference, of which L. B. Clapp of Brown and B. R. Willeford of Bucknell are the co-directors, will consider the undergraduate chemistry curriculum as a whole. Many colleges and universities have made extensive changes in their undergraduate programs in the last few years. Discussions of these and other possible programs will produce a real improvement in chemical education and will encourage the inauguration of other experimental approaches. Though there will be some platform presentations concerning new curriculums already in operation, this will be primarily a "working conference," involving several small groups considering various aspects of the curriculum.

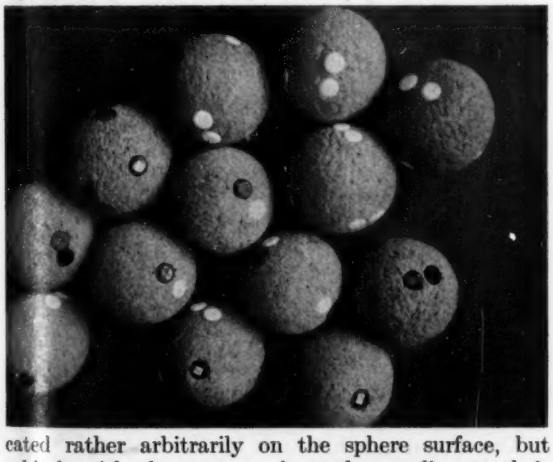
The aim of the conference to be held at Montana State College, Bozeman, will be to examine critically the philosophy and content of chemistry courses for non-science majors and to propose recommendations for making these courses a more effective means of providing a fundamental understanding of natural phenomena, their interpretation, and their impact on society. The conference, co-directed by A. B. Garrett of Ohio State and W. B. Cook of Montana State, will bring together twenty-five chemistry professors and five authorities from other disciplines for an informal working session, July 17–23. A report of both of these conferences will be made available to all who are interested.

R. T. Sanderson
State University of Iowa
Iowa City

Valence: A Laboratory Exercise for General Chemistry

Teachers may be interested in a new laboratory exercise on valence recently tested by 600 general chemistry students at Iowa. In this exercise, each student carefully examined each of a set of thirteen different atomic models, writing down certain pertinent observations and independently-reasoned conclusions about them.

The models are all Styrofoam spheres of like size ($2^1/_2$" d)[1] on which the outermost orbitals (s, or s and three p) are represented by enameled-headed upholstery nails, moistened with glue, and pressed into the plastic until the heads are flush with the sphere surface. White nail heads represent electrons, and black heads represent vacancies capable of accommodating electrons. A pair of white nail heads indicates a filled orbital and a pair of black nail heads, an empty orbital. A pair of one white and one black nail head represents a half-filled orbital—in other words, an unpaired electron. (Alternatively, the electrons and vacancies could be painted on the Styrofoam surface, either as black and white dots, or by some other designation such as minus signs representing electrons and zeros representing vacancies.) The empty orbitals are located rather arbitrarily on the sphere surface, but orbitals with electrons are located according to their known directional properties: two such orbitals, at opposite sides of the sphere; three, at the corners of an equilateral triangle around the sphere such that bond angles would be 120°; four, at the corners of a regular tetrahedron, angles 109°28′. A convenient way of locating three of the four corners of a tetrahedron on the surface of a sphere is to cut a circular hole in stiff cardboard, of diameter 0.94 times the sphere diameter. Mark at the edge of this hole the corners of an equilateral triangle circumscribed by the circular hole. Hold the card with the sphere fit snugly in the hole, and mark these same triangle corners on the sphere. These are three of the corners of the tetrahedron; the fourth can be located visually as exactly opposite the triangle.



For atoms with two, three, or four outer shell electrons (such as Be, B, and C), two models are provided, one representing the ground state, the other the valence state. For example, one model that might represent carbon shows an electron distribution of s^2, p_x, p_y, and the other, s, p_x, p_y, p_z. The thirteen models in the set have the outer electronic structures of H, He, Li, Be (2), B (2), C (2), N, O, F, and Ne. All the inert-shell and 18-shell elements are thus represented. Each model is labelled with a coded letter. A typical set of 13, for which the material cost was about one dollar, is shown in the Figure. One set suffices for each group of ten students.

This exercise was assigned only after completion of a series of classroom lectures to the students on electronic configurations and chemical combination. They were further prepared by a written description of the models and review of the principles of valence, issued to them several days in advance.[2] They were asked, after they had read this information carefully, to examine each model individually and record on a chart the following data: (1) code letter, (2) whether ground state or valence or both, (3) number of covalent bonds possible, (4) approximate bond angles expected, (5) number of coordinate covalent bonds possible, (6) whether electron donor or acceptor, (7) most probable formulas of its binary compounds (if any) with each of the other models (making no exceptions for possible intermetallic compounds where ordinary covalent stoichiometry is usually not observed), (8) underlining of the code letter of that element expected to become at least partially negative in the compound, and (9) a list of all actual elements (except transition elements) which each model might represent.

Time required for the completion of this exercise was about two hours. It gave students an opportunity to visualize and think directly about the electronic requirements for, and results of, chemical bond formation. The exercise also gave them a better appreciation of the significance of the electronic similarities underlying the classification of the chemical elements into groups of the periodic table. Reactions of both students and instructors were highly favorable.

Support of this work was provided in part by the National Science Foundation, Course Content Improvement Section, and is gratefully acknowledged.

[1] Obtainable in white, red, blue, and green from Star Band Co., Portsmouth, Virginia.

[2] Teachers wishing a copy of the full information and instructions for this exercise may obtain it by writing to the author.

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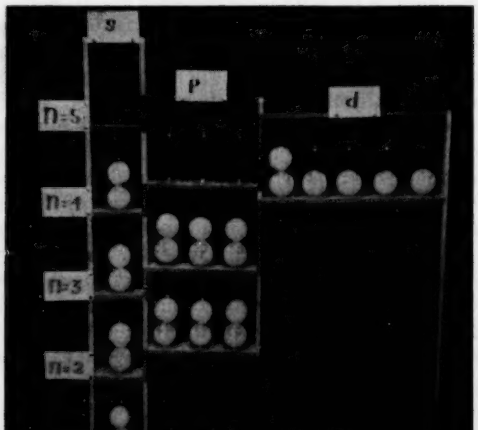
An Aid to Teaching Electronic Configurations of Atoms

A simple, crude, but effective visual aid, for demonstration during lectures on atomic structure, is shown in the accompanying photo. It consists of a series of shelves arranged to show qualitatively the differences in energy levels among the various atomic orbitals. Each orbital is represented by a beaker (400 ml, tall form) capable of holding two $2^1/_2$ in. diameter Styrofoam balls,[1] representing electrons. Each shelf represents a particular combination of principal and orbital quantum numbers and is of appropriate length to hold the correct number of beakers (orbitals). Each *s* shelf can accommodate only one beaker, each *p* shelf, three, each *d* shelf, five, and if the framework shown were extended to include *f* shelves, each would accommodate seven beakers. The shelf edges corresponding to each principal quantum level are painted a distinctive color: in the assembly illustrated, these colors are black (for $n = 1$), green, orange, blue, and red. This makes the stairstep arrangement of orbital quantum levels at the same principal quantum level easily visible to the students (although it does not show well in the photo).



Starting with the empty shelves and a supply of beakers and balls, one can demonstrate the building up of the atoms of elements of successively higher atomic number, starting with hydrogen, quickly and easily. When each alkali metal structure is reached, all the beakers (orbitals) of that particular outermost principal quantum level are placed on the shelves, and then filled in with balls as the atomic number increases across the period, observing the order of filling, *s-p-d-f*, and the rule that within a given sublevel, electrons do not pair until each available orbital contains a single electron. The electronic configuration illustrated is that of iron.

In this as in all such representations, the students should be told that the relative heights of the shelves (energy levels), only qualitatively shown here, represent the order of building up successive elements but *not* necessarily the order of electron energies within a given atom. For example, the significance of the slightly higher level of the 3*d* shelf in the photo is not that the 3*d* electrons of iron are less stably held than the 4*s* electrons, but rather that in the successive building up of atoms beyond argon, the more stable sublevel when the nuclear charge is 19 (K) and 20 (Ca) is 4*s*. However, with nuclear charge 21 (Sc) this order is reversed and from here on, 3*d* electrons are more stable than 4*s*.

As each electron is added, in the successive filling of atomic orbitals, it is helpful to tabulate on the blackboard the four quantum numbers that specify its position. For example, for the hydrogen electron, one would write:

Electron No.	n	l	m_l	m_s	Orbital Type
1	1	0	0	$^1/_2$	*s*

Even though, at the elementary level, students cannot be expected to comprehend fully, they can acquire in this manner a useful and logical picture of the significance and reasonableness of atomic structure. They need only accept the restrictions that l may have only values 0 through $(n - 1)$, m_l may have values of 0 through $\pm l$, and m_s only $\pm^1/_2$, together with the Pauli exclusion principle according to which no two electrons in an atom may have an identical set of four quantum numbers.

The support of this work by the National Science Foundation, Course Content Improvement Section, is gratefully acknowledged. The shelves were kindly constructed by Mr. J. H. Thomas.

[1] Inexpensive Styrofoam spheres in white, red, green, and blue can be purchased from the Star Band Co., Portsmouth, Virginia. The colored spheres have firmer surfaces, with greater resistance to abrasion.

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Are High School Chemistry Texts Up-to-Date?

During the development of the complete course in high school chemistry on film[1,2] produced by Encyclopaedia Britannica Films in cooperation with a committee appointed by the American Chemical Society and with funds provided by the Ford Foundation, it was necessary to become familiar with the high school texts currently used throughout the United States. This perusal of about fifteen texts published in 1954 or later provided some startling revelations.

Seemingly, most high school texts, with a few exceptions, present chemistry as it was taught in the first two or three decades of the twentieth century. In the majority of these texts the approach can be termed classical in nature with the emphasis placed on descriptive material. For instance, a typical approach for the first few chapters would involve chemical and physical changes, oxygen, hydrogen, water, simplified gas laws, solutions, atomic theory and laws involved, equations, and various simple stoichiometric relationships.

In the modern approach to the study of high school chemistry, descriptive material is utilized whenever it may be used to illustrate a law, theory, or concept. The emphasis is definitely upon broad generalizations which enable the student to understand and predict specific properties of a species rather than learning a lot of facts pertaining to an element or group of elements.

No one high school text presently known to be in print presents any phase of about thirteen per cent (13%) of the material covered in a more modern high school course; perhaps another thirty per cent (30%) of the material is presented in an up-to-date high school course in a manner entirely different from that used in existing high school texts; and approximately another twelve per cent (12%) of the material commonly included in a current high school course is covered very briefly, or merely mentioned in the high school texts.

Some of the points of distinction of a modern course are as follows:

The method of classification of matter. In only two or three high school texts is the method of Hildebrand and Powell[3] used as a basis of classification. In fact, methods of classification in high school texts are covered in a very cursory manner, if at all. In the modern approach to high school chemistry the importance of classification and its limitations should be emphasized.

The mole concept. Although most high school texts use the word "mole" (some do not even mention the word), the usefulness of the concept of a mole as a number has not been utilized. In the modern approach this concept is developed in such a way that its usefulness is apparent throughout the course. Is it so difficult for a student to recognize that Avogadro's number of particles, 6.02×10^{23}, is given a special name, "mole"? Do we not give the special name, "dozen," to the number twelve? Can we not say that a mole of oxygen molecules weighs 32.0 grams? In a modern course, problems are presented and solved by using the mole concept.

Bonding. In high school texts covalence and electrovalence are mentioned, but merely as isolated facts and not as a method of explaining properties of atoms and molecules. In the current approach to chemistry atomic and ionic radii have their place in this scheme correlating reactivities and crystal structure with experimental observations.

Water and solubility. Most high school texts do not offer any structure for water, or, at best, water as a linear molecule. In the modern course water is recognized as a "bent" molecule and a dipole, which is used to explain its peculiar properties and its ability to dissolve some ionic compounds. Students are fascinated with the simplicity of the explanation.

Acid-base theory. In some high school texts the Brønsted-Lowry concept of acids and bases is mentioned; in others there is no mention made; and in practically all secondary school texts the theory of Arrhenius dating from 1887 is used to explain the reactions of acids and bases. The two approaches may be controversial, and several years ago the author was a strong advocate of using only the Arrhenius theory to explain the reactions of acids and bases to high school students. However, as an experiment, certain high school classes were taught by their own high school teachers to determine whether or not high school students could understand and use the Brønsted theory, rather than the previously taught, limited Arrhenius theory. Very little, if any difficulty was encountered by the students. Therefore, the proton-donor and proton-acceptor theory with the attendant use of the concept of conjugate acids and basis is used to explain many chemical reactions. Incidentally, it is a very easy step from here to understand the Lewis theory (no high school text does this). Because of the advantages of the Brønsted theory in explaining hydrolysis, and, if the student expects to continue his study of chemistry in college, because the Brønsted theory is used to understand mechanisms of many organic reactions as well as those of non-aqueous solutions, this modern approach is more to be desired.

Equilibrium. On the high school level the textual treatment of equilibrium is "qualitative" rather than "quantitative." The effect of various factors on equi-

[1] *C. & E. News*, **35**, 44, 88 (November 18, 1957).
[2] *C. & E. News*, **36**, 9, 120 (March 3, 1958).
[3] Hildebrand, J. H., and Powell, R. E., "Principles of Chemistry," 6th ed., The Macmillan Company, 1952.

libria is usually presented, but not as part of the more general Le Chatelier principle. In some texts *p*H and the use of buffers are not mentioned. In the modern secondary school course this study is still "qualitative" but care is taken to differentiate between "rates" and "extents" of reactions. Greater emphasis is given to "equilibrium position," to the study of *p*H, and to the use of buffers.

Atomic structure. In very few high school texts is the approach the same as that used in up-to-date presentations. In the modern course the historical approach is minimized; and emphasis is given to the unpredictable path of the electron showing that "probability," not "orbit," best explains the facts. The Bohr energy levels are useful, but circular "orbits" are not considered tenable. Even the sub-levels can be easily learned in a descriptive manner. The student's interest is very intense in this phase of chemistry, and this interest can be used as a springboard to more serious study.

Symbols and nomenclature. Not one high school text has brought its nomenclature and symbols in accord with the most recent decisions of the I.U.P.A.C. in 1957. For instance, the symbol "Ar" is used to represent an atom of argon rather than "A"; and "iron(II)" is preferred over "ferrous." It is to be hoped these changes will appear in new editions.

Atomic, molecular, and ionic geometry. Some few high school texts portray the spacial arrangements of ions in ionic compounds (usually sodium chloride); still fewer mention the spacial structures of the atomic crystals; but not one seems to take into account the varying sizes of atoms and ions. Furthermore, different methods of ionic or atomic packing are not mentioned. In the modern course, these factors are constantly taken into account to help provide explanations of properties.

Mathematical problem solving. Many high school texts use a set formula in which a student may substitute values or they use the "proportion" method. The modern course stresses the "common-sense" approach in chemical reasoning commonly called the "factor-label" method.

Complex ions. Few high school texts even mention such a thing as a complex ion. An up-to-date approach utilizes these complex ions in explaining certain types of chemical reactions. Why, for instance, do aluminum and iron compounds form gelatinous precipitates? Why is aluminum amphoteric? The idea of aquo complexes can be used to correlate these facts. Indeed, a consistent approach to transition element chemistry incorporates the structure and properties of many different complex ions. Practical applications of theory help the understanding.

Valence concepts. In high school texts there seems to be a great deal of confusion as to what is meant by "valence." Valence is often confused with the charge on the ion. No high school text discusses the meaning of coordination number, and only one has anything about oxidation-numbers. In a modern high school course, various concepts are developed as to what is meant by electrovalence, covalence, coordination number, and oxidation-number.

Electrochemistry. No high school text discusses Faraday's Laws or the details of various well-known cells. Perhaps in the electrolysis of brine a high school text will state that the sodium ion changes to a sodium atom, which in turn reacts with water to produce hydrogen and sodium hydroxide. Such a mechanism is far from the facts. In an up-to-date course, with the mole concept as a background, the development is carried out quite simply. Simple oxidation-reduction reactions can be predicted and electrolytic reactions are explained.

The approach to chemistry in high school texts seems to be falling far behind our present-day concepts. The changes wrought by scientific development in the last several years have been proceeding at an ever-increasing rate. The high school chemistry teacher who has neither the time nor the energy to keep up-to-date has to rely on his text to provide the students with the basic facts. These so-called "facts" are often false or, at least, misleading; theories are presented that are outdated; and study material has been "watered down."

Teachers trained in the older classical approach to the subject matter of chemistry would find an examination of a modern college text a distinct help to them in understanding the study of chemistry as it is presented in many colleges. The time provided for a typical secondary school teacher of chemistry is little enough for his regular school duties, let alone keeping up-to-date in subject matter. Nevertheless, he should take the time to bring himself up-to-date in the newer concepts in general chemistry. A teacher could modernize his thinking by such means as: attending a summer institute; following certain television programs (i.e., Modern Chemistry on Continental Classroom), or by self-study.

Rather than continue with further dissertation on the subject, let us ask ourselves a question:

"What are we, as individuals, doing about the antiquity of information in current high school texts of chemistry and in bringing ourselves up-to-date?"

Correction: Availability of Movies on Chemical Subjects

The information carried on page 155 of the March, 1960 issue of THIS JOURNAL gave the impression that the three films by Linus Pauling, "Valence and Molecular Structure," were available for general use. Unfortunately this is not yet the case. These films were produced for NSF - supported institute programs, and at present the limited number of copies in existence are in heavy demand for use in the various NSF institutes. The hope is that NSF eventually will make these films available through commercial channels.

Personalities and Trends

After many years of inspired teaching and research at UCLA, Hosmer Stone will retire this year from formal activity. He always has been a well-liked staff member, showing constant, genuine interest in his students, who were often invited to his home for lunch or tea. Through the years he supported every effort in development of the chemistry department from its meager beginnings on the Vermont Avenue campus to its present location in the palatial structure in Westwood. In his advanced inorganic chemistry class, an introduction to research methods was explored by a series of rigorously penetrating experiments and projects. These required liberal usage by each student of the chemistry library. Among his many research projects has been experimentation with chromium(II) ion, much of which has been reported in the chemical literature through a series of papers. His activities have been varied and his contribution to the Southern California section of the ACS and PSACT will long be remembered, as will his sincere friendliness to faculty and students of UCLA and other California institutions.

After returning to Caltech from an extended lecture tour of Australia and New Zealand, Linus Pauling delivered a stimulating lecture on "Albert Schweitzer" at the Institute. In this lecture he told of the intellectual treat in the exchange of ideas of two Nobel prize-winners, whose Nobel prizes were awarded in widely divergent fields of endeavor. Underlying humanitarian interests have recently drawn them together in their thinking.

The Technische Hochschule Wien, Institut für chemische Technologie organischer Stoffe, is the Austrian residence of Norman Kharasch of USC this year. He returned to Los Angeles for a short business visit in February and then went back to Vienna to finish up his year there. During his absence, Walter Wolf of the University of Concepcion, Uruguay, is teaching some of his classes. Dr. Wolf has found a place of respect among the PSACT members by telling of his experiences at the University of Paris and in South America.

Raymond Bremmer of Fresno State College is a Fulbright Fellow at the University of Peshawar in Pakistan, during a year of sabbatical leave. Clifford S. Garner is on sabbatical leave from UCLA during the spring semester and summer. Saul Winstein of UCLA has been chosen a member of the Editorial Board of the *Journal of the American Chemical Society*.

Arthur Smith of Humboldt State College, the most northern of the California colleges, is taking a year of sabbatical leave to study with Robert D. Vold at USC. His wife and family are in England, where she is teaching outside of London. They will be united this summer while visiting laboratories in Europe.

Robert Henderson of Long Beach State College joined the steady stream of teachers going to Europe last summer. He will be on leave of absence during the second semester of this year and Don Simonsen will temporarily serve as acting chairman in his place. One of the most delightful locations for summer courses in chemistry is cool Long Beach. Students from all universities and colleges in the state are finding their way to Long Beach to take advantage of their summer offerings.

George Pimentel of UC presented a paper in Europe at the close of last summer. Nelson Smith returned to Pomona College after a year of sabbatical leave at Cambridge University and the University of Bristol. This year, Corwin Hansch of Pomona College is at the Institut für Organische Chemie in Munich. Both used PRF grants for this. Research at Pomona College is carried on chiefly during the summer under PRF, NSF, and Research Corporation funds.

Robert Maybury and his very capable co-worker, Richard Welsch, have been conducting a dramatic program of summer research and training of high school and junior college instructors at the University of Redlands. During the regular session, on Saturday, eight instructors are being trained in the use of the ultracentrifuge, infrared analyses, gas chromatography, and radio-tracer techniques, taught by men from industrial and other laboratories. A number of NSF Research Participation Program stipends are available for summer work at Redlands for qualified teachers in physics, biochemistry, and organic chemistry. A program of lectures has been instigated at Redlands with deeply serious intent. Wilfried Mommaerts of the UCLA Medical School, and director of the Los Angeles Heart Association Cardiovascular Research Laboratory, gave the first evening lecture in February on the chemistry of muscular contraction and expansion, a most fascinating evening for the many who attended. In May, Hans Neurath of the University of Washington Medical School will lecture on proteins. Funds from The American, California, San Bernardino County, and Riverside County Heart Associations are being made available to the University of Redlands in response to the dynamic insight captured by Bob Maybury in this work.

Jack Hileman of El Camino College will renew his graduate work, this time on a NSF award at UCLA for one year. His capable work as secretary of the southern section of PSACT has been appreciated by all PSACT members. The University of San Francisco reports that Robert Sewald is continuing his research on the synthesis of fluorescent biological tracers, supported by the U. S. Public Health Service. Mel Gorman spent the summer at UC on a NSF faculty fellowship. He has also been elected to the council of the ACS, representing the Division of the History of Chemistry. G. E. McCasland attended various scientific meetings in Europe. A NSF Undergraduate Research Program, directed by chairman William Maroney, helped to push student research to a new peak. Arthur Furst of Stanford University and the University of San Francisco delivered papers and lectures in Rome, Milan, and other European cities.

From the lower end of California comes news of the move of the San Diego State College Chemistry Department into its huge new laboratory. Among the facilities are 22 large laboratories with 24 student stations in most of them. Also there are four graduate research laboratories with six to eight student stations each. The research activities include a contract from Convair Scientific Research Laboratory under Drs. Malik and Rowe for HF Kinetic Rate Studies. Dr. Sheppard received a grant from Research Corporation for environmental studies of oxidation-reduction reactions. Lionel Joseph obtained a grant from the San Diego County Heart Association for a continuation of studies of vasodilatory agents. This was supplemented by a grant from the U. S. Public Health Service for the study of benzimidazole derivatives as anti-tumor agents. Dr. Hellberg received a grant from the Research Corporation for studying possible methods of arylating cyclanones. He also held a contract from Convair Scientific Research Laboratory for investigation of hydrolysis rates of alicylic esters. Drs. Landis and Wadsworth are continuing their work on the solution chemistry of titanium financed by an additional grant from Convair Scientific Research Laboratory. Dr. Wick is continuing his studies of carbohydrate metabolism under a five-year grant from the U. S. Public Health Service.

Two new members were added to the Sacramento State College staff this year, Dr. Rodney Sime, a physical chemist, who did his graduate work at the University of Washington, and Dr. Arthur Williams, an organic chemist from the Colorado School of Mines, who did his Ph.D. work at UC, after which he worked with the Cutter Laboratories. Next year a new nuclear chemistry laboratory will be housed in a separate small building.

At San Jose State College, Mrs. Vera Diehl received the first M.S. degree. The M.S. program, now in its second year, cur-

rently has 22 students enrolled, 15 of whom are devoting full time toward attainment of this degree. Laurence Wilson has been added to the staff in inorganic chemistry. He received his Ph.D. from the University of Washington. The Research Corporation awarded Ralph Fessenden a grant for a study of organic silicon compounds. The chemical instrumentation conference at New York University was attended last summer by Bert Morris.

Conferences attended by members of the staff of UC, Santa Barbara, were the international Symposium on Fluorine Chemistry in Birmingham, England, by G. O. Pritchard, the ACS meeting in Atlantic City by H. L. Nyquist, and the American Vacuum Society Meeting by G. H. Miller in Philadelphia. The Research Corporation granted Dr. Nyquist funds for research on anti-cancer agents.

JOHN LEO ABERNETHY
Editor of PSACT Proceedings

UNIVERSITY OF CALIFORNIA,
LOS ANGELES

ChemEd

LETTERS

To the Editor:

It is often necessary to have a reliable standard cell for calibrating vacuum tube voltmeters, *p*H meters, electrometers, etc. We have found the following cell very convenient for the purpose:

Hg, Cd | $CdSO_4 \cdot {}^8/_3\ H_2O$(s), saturated solution, Hg_2SO_4(s) | Hg | Hg_2SO_4(s), saturated solution, $ZnSO_4$(s) | Zn, Hg

This consists of the Clark's cell in opposition with the Weston cell and has at t°C an emf of $E_t = 0.40858 - 0.00115\ (t-20)$ for temperatures below 39°C.

The construction is as shown in the diagram.

B. A. SHENOI
J. RAJARAM
K. R. NARASIMHAN

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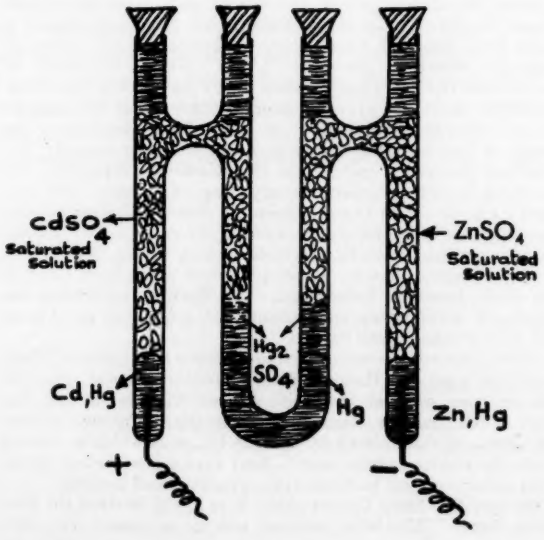

To the Editor:

The article, "Weight Titrations Revived" by J. M. Thoburn, **36**, 616 (1959), prompts me to send you this note. For over a year now I have been making weight titrations using a polyethylene wash bottle of about 130 ml capacity which weighs less than 25 g empty. These bottles cost about a dollar apiece and are obtainable from most scientific apparatus retailers. They are very convenient to use. No drops cling to the tip. The small tip allows delivery of minute drops. There is no stopcock to lubricate or stick. They may be put away with the titrant still in them without fear of attack. They stand on a balance pan without any tendency to roll. They are almost ideal weight burets.

BART PARK

MICHIGAN COLLEGE OF MINING AND TECHNOLOGY
HOUGHTON

EDITOR'S NOTE: A letter from Mr. Edward T. Radley, at present studying at the University of Missouri, makes the same suggestion.

To the Editor:

May I respectfully point out an error in the identification of the languages illustrated by the October "H_2SO_4" cover? While "oil of vitriol" can certainly be classified as English, "sulfuric acid" is, of course, American. "Sulphuric acid" is used exclusively in this country and probably seems as alien to Americans as the alternative spelling does to chemists this side of the Atlantic, even allowing that we agree on the spelling of "phosphorus."

It would be interesting if any of your correspondents can trace the origin of this and other deviations, such as aluminum-aluminium, cesium-caesium, lutetium-lutecium, etc. Perhaps in the case of sulphur (derived from the Latin "sulfur") the American form has been influenced by the French of Louisiana.

D. C. CORNISH

BRITISH SCIENTIFIC INSTRUMENT RESEARCH ASSOCIATION
CHISLEHURST, KENT, ENGLAND

Report of the New England Association of Chemistry Teachers

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West Springfield High School
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Atoms, Fire, Waves, or What?

What is an atom? The word atom, meaning indivisible, has its origin in the Greek culture; Democritus (460 B.C.) is given credit for the description of nature as composed of atoms. The stimulus for the idea is not exactly known, but some attribute it to his teacher Leucippus.[1] Others point to the general atmosphere of speculation on subjects such as the origin of matter which was then rife. Historians usually agree that Democritus extended the prevailing thoughts of his time, although he performed no experiment to prove the existence of his fundamental particle—he only imagined it to exist. His reasoning is clear enough: A piece of paper can be cut in half, and in half until it cannot be cut in half again, no matter how sharp a tool is used. There seems to be no reason why such an atom cannot exist.

The genius of Democritus is not so much that he postulated the existence of the atom but that he stated for the first time that atoms moved within matter in a void or vacuum. An analysis of how he developed his idea gives us clues as to what science is and how it advances: He summarized the known beliefs of his time; he made use of the known tool of science—reasoning; he developed what we can call a model of the atom and with this model he postulated the atom's properties. Earlier philosophers had thought of the known elements as fire, earth, air, and water and had spoken of the fire as moving out of one body into another. Democritus thought that the different elements must have different shapes. He reasoned that because water slipped easily, its atom must be round and smooth. One can predict that if smooth water is added to rough atoms, the rough spots would be filled in and the rough atoms would become smooth. We can see this work when we add water to cupric sulfate crystals, but Democritus would point to the working artisans and say, "Stir, grind, and heat the indigo plants to smooth out the dye."

About a century later Aristotle, a student of Socrates and Plato, developed a hypothesis that matter was continuous. Though he used much the same background as Democritus had used, and even had the advantage of knowing Democritus' theory, he reasoned differently. With equal justification, he decided that matter could not only be split to the same point as Democritus' atom but could be split forever thereafter. Aristotle made his model more convincing by adding to it the concept of opposites. Both Democritus and Aristotle were aware of the continual struggle between opposites (day and night, light and dark, wet and dry, etc.), but it was Aristotle who included it in his explanation of nature. He reasoned that sets of opposites, together with *prima materia*, composed the material world. The *prima materia* was the force between the sets of opposites. Thus we may consider the following diagram (Fig. 1) as the chemical model of Aristotle's theory and essentially the one that was most respected for the next 2000 years![2] The qualities of hot, cold, wet, and dry could be imposed upon the prime matter in any amount, by a continuous flow. For instance, if two dry sticks are rubbed together they become hot and will produce fire. When heat is taken from air which contains moisture, the product is water. It is possible to add fire to earth, driving out cold and giving a product which will be a metal somewhere between water and earth.

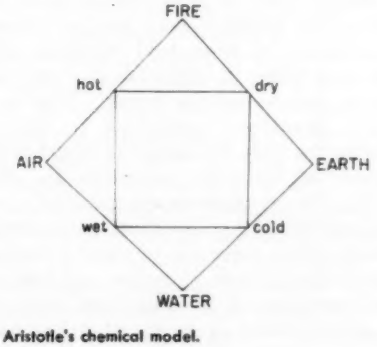

Figure 1. Aristotle's chemical model.

The models of Aristotle and Democritus are products of pure thought without any reference to validation by experiment. As products of reason both are equally reasonable. Aristotle's model was accepted almost completely because it gave the best summary of the previous thoughts and observations. It made predictions better than Democritus' model.

[1] LEICESTER, HENRY, "The Historical Background of Chemistry," John Wiley and Sons, Inc., New York, 1956, p. 18.

[2] READ, JOHN, "Through Alchemy to Chemistry," G. Bell and Son, Ltd., London, 1957, p. 17.

Two Centuries of Slow Progress

During the next 2000 years, chemistry advanced as follows: Artisans began to use Aristotle's model to make predictions, then tested the predictions. Some of them, who called themselves "Alchemists" tried to find the correct amount of fire to add to earth to produce the metal gold. The Chinese alchemists strove to make gold to gain longevity, because gold did not rust. Western alchemists wanted to replenish the treasuries of the kings who had set up their laboratories. Most of these alchemists were good experimenters; so their work resulted in new products like gunpowder, alcohol, medical drugs, and special laboratory equipment.

As the alchemists found new substances, new ideas developed concerning the *prima materia*. Each experimenter required new modifications of Aristotle's model to fit the new substances that he had isolated, for the original model could not satisfy all the necessary requirements. Thus, in about the eighth century, Geber proposed a modification based upon a *Tria Prima*. The three fundamental properties of his model were: metallic, represented by mercury; loss of metallic, represented by sulfur; and stability, typified by salt. Thus he argued that copper had some sulfur in it to give it the yellow color, but it was not pure enough. High purity would result in tin, iron, and other metals. The task of the alchemist was to get the black fire of sulfur (sometimes referred to as the philosopher's stone) into the earth in the correct ratio. Geber's theory retained the principle of continuous matter, but he added the concept that certain qualities can be imposed upon matter. This gave a new challenge to the alchemist.

Two major difficulties with Geber's model were its dependence on the continuous nature of matter and its emphasis on spirit-like properties. In an extension of it near the end of the seventeenth century, Stahl proposed that all matter is composed of the spirit of fire, called phlogiston, and of an ash called calx.[3] The difference between various substances was dependent upon the amount of phlogiston that each substance contained. Stahl helped to revive the atomist viewpoint that matter was discontinuous, for he reasoned that phlogiston and calx were held together by forces similar to those later thought of as "gravitational." Therefore he had to assume atoms. This model met with almost immediate acceptance by all chemists. For the first time they could explain the action of fire. The emphasis on spirit-like properties was eliminated in favor of a theory requiring quantitative amounts of phlogiston and calx. As a result, attention was focused on combustion and reduction of metals, and corrosion was recognized as a slow process of combustion. The new model summarized previous knowledge and made predictions for chemists to check. Stahl had generalized from the known data, as had Aristotle, Geber, and Democritus. But more significantly he took data and observations from experiments, and generalized from them. Stahl had experimental proof, not just armchair philosophy. For example, if a stick is burning, the phlogiston is leaving at such a rate that it is hot. When iron gives off its phlogiston, red rust is the result. If either the burning stick or the iron is placed in a closed container, the phlogiston will stop going off as soon as the container becomes full of phlogiston. If a zinc calx is heated with charcoal (a substance which contains a lot of phlogiston) the product is metallic zinc.

Stahl's model was used for about a hundred years. In this case, as in many other cases, this was much too long, although the success of Stahl's model is demonstrated by the growth of chemistry in the eighteenth century. Motivated by it, practicing chemists made great strides in an effort to catch and isolate phlogiston. The result of their effort was the discovery and isolation of many gases and a study of their properties. The work of great phlogistonists such as Boyle, Cavendish, Priestley, Black, and Scheele advanced chemistry.

In the 1770's Lavoisier was concerned with two problems of the phlogiston model.[4] How can all the reducing gases be the same phlogiston? How can one explain the gain in weight in burning iron and the apparent loss of weight in burning wood? Lavoisier could explain the difficulties if combustion were considered to be the combination of oxygen with other matter. Lavoisier's model can best be described by the quantitative relationship: Matter plus oxygen yields material oxide.

Lavoisier's model was needed when the experimental data extended beyond the scope of Stahl's model. It was conceived in the author's mind with the clues provided by nature. The validity of the model arises from its explanation of and its prediction of nature.

Atoms: Units of Elements

During the thirty years following the work of Lavoisier, quantitative data were gathered concerning the nature of matter. Prominent in this activity were: Gay-Lussac, who showed that gases react in volume-ratios of whole numbers; Berzelius, who developed equivalent-weight relationships between substances; Richter, who postulated the definite proportion by weight relationship from his studies on oxides. Their data were best summarized and generalized by an English school teacher named Dalton. Early in the nineteenth century he described a new model based upon the discontinuous nature of matter. He postulated:[5]

Chemical elements are composed of atoms.
Atoms can neither be created or annihilated.
Atoms of the same element are identical and have the same mass.
Atoms of different elements have different mass.
Combinations occur between atoms in whole number ratios.

Notice that these postulates had been confirmed and discovered, not by Dalton, but by many other chemists. All except the second postulate can be attributed to an individual or group that was studying that specific postulate. The second postulate formulates the law of conservation of matter, a generalization not included in any previous model. From it we can write chemical reactions and predict what the products will weigh. This postulate also gives theoretical evidence for the law of definite proportions. This generalization was as great as Aristotle's and Stahl's. Furthermore, Dalton's model of the atom is based more upon experimental data than

[3] FRENCH, SIDNEY, "The Drama of Chemistry," The University Society, New York, 1937, p. 27.

[4] LEICESTER, *op. cit.*, 143.

[5] "Chymia No. 1: Annual Studies in the History of Chemistry," T. D. DAVIS, *Editor*, University of Pennsylvania, Philadelphia, 1948.

any of the previous models. Its usefulness may be judged by its success in predicting from formula such diverse items as the amount of iron recovered from smelting processes, and the best method to prepare a new element.

The Dalton model immediately challenged scientists with important questions: How do atoms stay united with their own kind or with other kinds of atoms? (Newton's gravitational forces are inadequate). What is the explanation of multiple proportions? Why is the formula CO_2 more correct than C_2O_4?

The explanation of these questions and of others of a more complex nature reached a climax after many contributing discoveries in chemistry and physics. The chemists were struggling to arrange the elements in an order that would facilitate understanding and prediction, while the physicists' emphasis was on explaining the energies between atoms. The work of Dobereiner, Newlands, Meyer, and Mendeleev characterizes the work of the chemists. It is the work of the physicists that established the background which Bohr used to develop an even more complete model of the atom. Following is a list of the more significant discoveries known to Bohr.

Faraday in 1844 suggested from the results of his studies of conduction and of electroplating with chemical solutions, that electricity was carried by atoms with a charge.

Crooks in 1874 developed and used the cathode ray tube to show that these rays were capable of exerting force. He concluded that they were material-like.

J. J. Thomson in 1897 proved that the cathode ray consisted of negatively-charged particles with a mass ratio about $1/2000$th that of the hydrogen atom. Thomson pictured the atom as a solid mass with electrons imbedded in the mass. His model has been called the "raisin bun" or "rice pudding" model.

Becquerel in 1896 showed that salts of uranium gave off a radiation that penetrated matter and darkened a photographic plate. He explained the phenomenon as radiation of X-rays, similar to Thomson's electrons.

Rutherford in 1899, working with materials that the Curie's had shown could be isolated, separated radiation into three types: the positive or alpha particle, the negative or beta particle, and the neutral or gamma wave. His careful experimentation enabled him to show that the alpha particles were ionized helium gas. Rutherford also showed that most alpha particles penetrated gold foil but that a few were scattered by it. From these experiments he extended Thomson's atom model to say that the electrons are not imbedded within the mass but are separated from the nucleus with a void between. Rutherford's model helped physicists to understand electricity, but its greatest accomplishment lay in its challenge to the scientist to find order in the arrangement of the electrons.

Moseley in 1913 observed that X-rays produced a characteristic frequency that varied from one element to the next in a regular shift. Moseley reasoned that each succeeding element in the periodic table had one more electron than the previous one.

Planck in 1900 postulated that radiation of all energies is emitted or absorbed in discrete bundles of energy called quanta.

In 1905 Einstein explained the photoelectric effect by assuming that the energy absorbed by an emitted electron is measured in quantized units, therefore is independent of the intensity of the incident light.

Bohr's "Working Model" of the Atom

In 1915 Niels Bohr working with Rutherford at the University of Manchester, conceived an order in the electrons outside the nucleus of Rutherford's model. His efforts were centered on explaining the spectra of the elements, for Rydberg had developed a set of empirical rules to predict them. Bohr attempted to explain these results and those of Balmer and others by postulating:

The hydrogen atom consists of one negative electron revolving in any one of a large number of possible orbits about a central massive, singly-charged positive nucleus. The particles will not obey Newtonian mechanics.

The only orbits permitted are those in which the angular momentum of the electron is equal to whole number ratios of Planck's constant. $mvr = \frac{nh}{2\pi}$

No radiation is emitted as long as the electron remains in a given orbit, but when an electron changes orbits a radiation is emitted of a frequency which is equal to the ratio of its energy divided by Planck's constant. $\nu = E/h$

This model includes no prediction of the process of radiation.

Bohr gives credit for each of the first three postulates to various scientists who made the discoveries or to the many who were trying to explain spectra. This was the prevailing problem of the day for every young and ambitious physicist. Bohr's contributing postulate was the definition of the limitation of the model. Bohr realized as no one else did that only a portion of nature was explained by the model. He was concerned with the energy and orbits of the electrons about the nucleus, but he could not explain the reason why or how the process of radiation occurs. No one has since. With this model we can calculate the wavelength and frequency of the emitted light to agree with the experimental data of Rydberg, Balmer, and Paschen. But as a good model should, Bohr's model predicted spectra lines in the ultraviolet and infrared region. These spectral lines were later verified.

Chemists immediately used the model to show the relationship of electrons to the periodic arrangement and to valence. G. N. Lewis of the University of California visualized a model which placed the electrons at the corners of a cube in order to help predict properties of the element. Using Moseley's method of assigning order to the elements by the number of electrons and using Bohr's model of the permissible orbits, Lewis postulated a model that has been most useful to the chemist in predicting formulas of compounds and explaining ion formation. Models such as this help chemists predict the properties of elements.

Bohr's model was limited because it did not predict accurately the spectral lines for the elements heavier than lithium. Many attempts were made to patch up the model to make it work for other elements. It became necessary for each element to have its own correction factor to make the prediction agree with experiment. The use of elliptical orbits instead of circular orbits is one successful modification. A very useful model uses circular and elliptical orbitals with a maximum of two electrons per orbital—still grouped at energy levels as Bohr calculated. The situation reminds us of the similar situation involving modifications to the Aristotle models.

Matter and Waves

DeBroglie in 1924 pointed out two major improvements in the classical description of the spectrum of light from metals. The first was that the particles of matter behaved as waves of energy, second, that the orbits of Bohr confined the particle to a definite location. From these developments DeBroglie postulated a model

of the electron as a wave, the length of which stretched around the nucleus. (Fig 2).[6]

Figure 2. DeBroglie's electron model.

The wave amplitude represents the probability of finding the electron at that location. DeBroglie's wave equation $\lambda = {}^{h}/_{p}$, represents a very useful model in working with diffraction of X-rays. The diagrams shown are misleading as no visualization can be made of a wave that extends to space. But the model serves to give some information dealing specifically with wave diffraction of particles through a crystal. However DeBroglie does not give a better description of the electron. It was left to Schrödinger to develop a model useful to the chemist's predictions.

Schrödinger based his model of the atom on the postulates of DeBroglie. He predicted that the wavelength is associated with the movement of a particle. Schrödinger was familar with the mathematical description associated with a variation of the wave amplitude throughout space. This description is given by a second order differential equation as shown by Hamilton nearly a century ago. Thus Schrödinger's model of an atom is represented by:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{4\pi}{h^2}\,2m(E - P)\psi = 0$$

where m is the mass of the electron; E, the total energy of the electron; P, the potential energy; h, Planck's constant; x, y, and z, rectangular coordinates that locate the electron in three dimensions; ∂^2 refers to mathematical process to solve for ψ, a quantity called the wave function or the probability amplitude.

The Schrödinger equation yields three solutions for each of the infinite number of states in which an electron can be located. This is no more mysterious than the algebraic equation, $x^2 - 3x - 4 = 0$, which yields results of $x = -4$ and 1.

The solution of the Schrödinger equation yields expressions in terms of quantum numbers. These values can be referred to as: n representing the probability density of the electron, l representing the angular momentum of the electron, and m representing the orientation of the angular momentum. There are two prevailing interpretations of this model. One is that the ψ can represent the probability of finding the electron at a given location. The second interpretation is that of picturing the electron spread out as a fog, with the density of the fog varying and reaching a maximum at Bohr's energy levels. Schrödinger's model will do all the work that Bohr's model could do and more. The model allows the chemist to predict the stability of any compound, including the 105th combined with the 121st.

Schrödinger proposed his model in 1926 and used it to give predictions of spectra. But as measurements became more accurate, at many positions in the spectrum where one line was expected, more than one was found. This was accounted for by assigning a number called spin to the electron. Pairs of electrons could have opposite spins. It turned out this was a poor notation, for how can a fog spin? The visualization in itself is bad. Dirac in 1931 gave theoretical reasons for the inclusion of a fourth variant in the Schrödinger equation. Dirac treated the wave relativistically. Thus he did not change the model, but expanded it to include a solution yielding four conditions for the electron, the n, l, m, and s values. Pauli interpreted these values to develop the same periodic arrangement of the elements that previous chemists had arranged without theoretical reason. This part of the solution in itself is a model helpful in predicting chemical binding and properties of the elements.

No model is all-inclusive in its description of nature. As models of the atom developed from Democritus to Dirac, they have been postulated from creative thought based upon observations of nature. As scientists strove for more accuracy, we have come to a more difficult description with which to visualize a model for nature. The description has evolved from wordy sentences to the more definite but more abstract mathematical descriptions. The present models are not to be visualized. They extend science beyond the common-sense experience and observations of the non-specialist.

It now must be asked with good intentions, "What are the limitations of Dirac's model?" The answer is that it works to an accuracy of eight or more significant figures with the electron, but it makes poor predictions of the happenings in the nucleus. "What is the more general model?" Some say Heisenberg has the solution. Heisenberg postulated in 1926:

To every observable there corresponds an operator (an operator is a procedure in matrix algebra and an observable is any number that can be observed.)

The only possible values which are the measurement of an observable whose operator is P are the eigen-values (little p) for the expression:

$$P\psi i = p\psi i$$

(when you make an observation, the observation is restricted before you make it.)

When a system is in state ψ, the expected mean of a sequence of measurements of the observable whose operator is P is given by the expression:

$$\langle p \rangle = \iiint_{-\infty}^{\infty} \psi^* P \psi \, dx\, dy\, dz$$

If ψ is given now, its value at a later time is a solution of the expression:

$$H\psi = ih/2\pi \frac{\partial\psi}{\partial t}$$

Heisenberg's model is not meant to be visualized. It is meant to give specific solutions to specific problems. The answers will not be definite but will give probability values. It is the challenge to the present generation to develop this model.

Notice that scientists started with a feud over the continuous or discontinuous nature of matter. Present models avoid this and claim matter to be both continuous and discontinuous, stating that matter is both particle-like and wave-like.

[6] BLANCHARD, C. H., ET AL., "Introduction to Modern Physics," Prentice-Hall, Inc., Englewood Cliffs, 1958, p. 179.

Chem Ed

BOOK REVIEWS

General Chemistry: A Systematic Approach

Harry H. Sisler, University of Florida, *Calvin A. VanderWerf* and *Arthur W. Davidson*, both of the University of Kansas. 2nd ed. The Macmillan Company, New York, 1959. x + 851 pp. Figs. and tables. 16 × 24 cm. $7.95.

This second edition of the 1949 version offers a fund of information that, if covered completely, would be sufficient for a three-semester general chemistry course. In this regard, the text provides a wide range of individual subject matter selection. In general appearance, chapter order, and subject matter, the revised edition is very similar to the first.

Most of the chapters have been rewritten somewhat, particularly in providing up-to-date data. Several chapters, notably the one on Solutions of Electrolytes, have been rather completely redone. Arrhenius has been relegated to a brief historical comment with the major portion developed by means of the Brønsted-Lowry concept. It does, however, seem somewhat inconsistent to utilize the H^+ ion in the discussion of the common ion effect and the *p*H scale after writing about the H_3O^+ ion, even though H^+ is designated "an abbreviated form."

A completely new portion has been added to one of the chapters on Atomic Structure involving the nuclear reactor, nuclear fusion, and the peacetime uses of atomic energy.

In the chapter pertaining to carbon and silicon, the explanation of resonance has its place in the body of the text rather than in a footnote. The chapters involving organic chemistry have been reworded, revised, and rewritten in view of more modern developments.

In the section introducing metals, some of the repetitious material has been deleted and four pages of a "Glossary of Metals" have been added. These tables contain such useful information on metals as the physical properties, U. S. consumption, average costs per pound, and uses.

Throughout the text new diagrams have been used, and some older ones deleted; there is an increase in the number of questions and problems following various chapters, which provides greater variety for study material. Some portions were rewritten in the interest of clarity and simplicity of explanation. Tables giving ionization potentials have been rounded off to one decimal place and brought up to date, and the historical developments have been minimized.

The text offers a pleasant balance between theoretical and descriptive material, and is a few pages shorter than the first edition. It should be an even more usable book for general chemistry classes.

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Reviewed in This Issue

Harry H. Sisler, Calvin A. VanderWerf, and *Arthur W. Davidson*, General Chemistry: A Systematic Approach
Robert Schwarz, Translator, Liebigs-Wöhlers Briefwechsel
Gregory H. Wannier, Elements of Solid State Theory
James Taylor, Solid Propellant and Exothermic Compositions
Hans Eichner and *Hans Hein*, Reading German for Scientists
H. M. Finniston and *J. P. Howe*, Editors, Progress in Nuclear Energy Series V: Metallurgy and Fuels. Volume 2
The Tintometer Limited, Colorimetric Chemical Analytical Methods
Brage Golding, Polymers and Resins
A. L. Mndzhoian, Editor, Syntheses of Heterocyclic Compounds. Volumes 1 and 2, translated from the Russian by *A. E. Stubbs*
Stephen Zamenhof, The Chemistry of Heredity
Morris H. Shamos, Editor, Great Experiments in Physics
Robert Jenness and *Stuart Patton*, Principles of Dairy Chemistry
G. N. Whyte, Principles of Radiation Dosimetry
J. W. Perry, Scientific Russian Without Tears
John R. Young, An Experimental Inquiry into the Principles of Nutrition and the Digestive Process
E. Segrè, Editor, Experimental Nuclear Physics. Volume 3
William Haynes, Brimstone: The Stone That Burns
J. A. Pople, W. G. Schneider and *J. J. Bernstein*, High-Resolution Nuclear Magnetic Resonance
E. S. Makarov, translated by *E. B. Uvarov*, Crystal Chemistry of Simple Compounds of Uranium, Thorium, Plutonium, Neptunium

Aus Justus Liebigs und Friedrich Wöhlers Briefwechsel in den Jahren 1829–1873. Auf Grund der von A. W. Hofmann besorgten zweibändige Ausgabe

Gekurzt von *Robert Schwarz*. Verlag Chemie, Weinheim/Bergstrasse, Germany, 1958. 406 pp. Two portraits. 15 × 21 cm. 24.50 German marks (approximately $6).

Liebig (1803–1873) and Wöhler (1800–1882) were close friends for more than forty years. Their first contact came through scientific controversies, but when they met face to face they took to each other at once. They began to correspond; the initial "Herr Professor" and "Herr Doktor" were soon replaced by the informal "Du." More than 1500 letters passed between them from 1829 until Liebig's death in 1873; the last items are dated within two weeks of this event. Neither man knew that the other had carefully preserved his letters.

When Liebig's will was read, it was found that he had left the Wöhler letters to his grandson, an ardent collector of autographs. During his last year, when Wöhler was leading what he called a "cloistered" life, he requested that his letters to Liebig be sent to him for perusal. He read them along with his own collection of the corresponding letters from Liebig, and marked what he thought might be of some importance to the history of chemistry and worthy of publication.

These notations were followed by A. W. Hofmann, who with the assistance of Wöhler's daughter went through the entire correspondence and prepared the two-volume work which appeared in 1888. This was widely read for many years, but eventually it became a fairly rare item. The present editor, fully appreciative of the unique merits of this correspondence, realized that much of it had outlived its usefulness, and accordingly deleted that portion from the text. The result is the present one-volume edition.

All sorts of matters were included in these letters, including family affairs, travel plans for joint vacations, comments on various personalities, and other personal communications. The reader will find here also, however, insights into the genesis of some of the great chemical feats of these eminent chemists. He will get an idea of the tremendous burden of work which they voluntarily assumed as laboratory men, teachers, and writers. Regularly they expressed their disgust with all things chemical and noted their periodic attacks of "semester fatigue," the inevitable result of long hours in poorly ventilated laboratories and at writing desks, where they toiled without benefit of secretaries or typewriters.

The divergent personalties of the two men are plainly seen in the letters. Liebig, fiery, impetuous, and ruthless in his treatment of those who did not agree with him, was often admonished by the calm, even-tempered Wöhler, who though only three years the senior talked more like a much older brother. This disparity in character may well have been the basis of this unusual friendship in which two men, though working in the same science and often on the same topics, never showed

the slightest envy or jealousy of the success of the other.

The present editor has added some valuable comments regarding certain now obscure points and personages. The deletion of whole letters or paragraphs occasionally leaves the reader in the air, but this is due to the effort to compress the tremendous mass of material into a book of average size. The German is not difficult and can be handled by most chemists and students whose competence in this language is what it should be. Excellent portraits of Liebig and Wöhler are included; it would have been nice to see a facsimile of a page written by each of them.

The reviewer has read these letters many times and recommends them to those young chemists who have not had this pleasure. They will learn much from these behind-the-scenes glimpses into the lives, activities, and characters of the Damon and Pythias of chemistry.

This advice will probably be heeded by only a few, but here again the phenomenon is not a new one. On August 6, 1841, Wöhler wrote to Liebig: "I certainly am not in favor of having every accidental observation that is not followed up being regarded as a discovery and anxiously considered and cited. However, a person must be essentially concerned about the history of his science. The young people nowadays study nothing except the textbooks and the handbooks; the study of sources is neglected more and more. Thus a conceited young man puts into print as an important discovery that palladium is malleable, as though Wollaston had worked palladium by some means other than its malleability—and the editor of the Journal allows this to be printed without uttering a syllable about it. This happens hundreds of times."

To which can only be added that this plea for a proper consideration of the history of our science will doubtless continue to be voiced as long as there are old and young chemists.

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Elements of Solid State Theory

Gregory H. Wannier, Bell Telephone Laboratories, Murray Hill, New Jersey. Cambridge University Press, New York, 1959. vi + 270 pp. Many figs. 14.5 × 21.5 cm. $6.50.

In the author's preface he says, "This book represents an attempt to provide a coherent and brief outline of the theory behind present-day solid state physics. It is aimed at advanced students or scientists with good all-round knowledge, but does not assume previous acquaintance with this specialty. An effort was made to produce a book which can be read from cover to cover and which reveals, if read in this way, some of the main ideas specific to solid state physics. In order to achieve this, severe limitations in scope had to be accepted. Some topics of current interest are missing altogether, and others will be found in skeletonized form only. To minimize this latter inconvenience a bibliography of comprehensive articles is appended to each chapter through which the topics discussed in the book may be opened up fully. Also the problems at the end of the chapters will help to round out any particular discussion which may appear too terse to the reader."

This is an admirable description of what the book accomplishes; a reader with requisite mathematical background will find reading of the volume profitable, since the exposition is clear and the organization very well done.

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Solid Propellant and Exothermic Compositions

James Taylor. Interscience Publishers, Inc., New York, 1959. vii + 153 pp. 12 plates, 21 figs., and 27 tables. 14.5 × 22.5 cm. $4.25.

The author states in his preface that his objective in writing this book was "to give a picture of the wide range of chemical compositions which have been developed as sources of energy for various applications and also to describe the applications." He also states that "the material is largely derived from work which has been carried out in the Nobel Division Laboratories of Imperial Chemical Industries over the last thirty years—but is supplemented by information from other published work." It is therefore to be expected that the book will be somewhat slanted in the direction of work carried out in I. C. I. Thus we find that twenty-five pages of the text are given to a chapter on Low-Temperature Gas-Producing Reactions Based on Nitrites, and the 'Hydrox' Blasting Device and to one on Power Cartridges, whereas only fourteen pages are given to the chapter on Propellants.

Considerable attention is given to the mechanical details associated with the application of exothermic compositions and there is a discussion of the principles of rocket motor operation. However, there is little reference to the most recent developments. As the title indicates the author concerns himself only with reactions occurring in the condensed state, i.e., as solids or liquids. As a matter of fact the chapter on rocket motors gives only about a page to liquid propelled rockets and most of that is to liquid monopropellants. Such substances as hydrazine, unsymmetrical dimethyl hydrazine, the hydroborons, for example, are not even mentioned. Thus, it may be observed that this volume does not provide a well-balanced or modern treatment of the field. However, the volume contains some very interesting information and would be a useful addition to the library of the chemist who is interested in the fuel or propellant field.

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Reading German for Scientists

Hans Eichner and *Hans Hein*, both of Queen's University, Kingston, Ontario. John Wiley & Sons, Inc., New York, 1959. xi+207 pp. 14.5 × 22 cm. $5.25.

Whether used in classrooms or for self-instruction, this new textbook offers both efficiency and effectiveness. Intentional omission of any instruction aimed specifically toward *writing* or *speaking* German saves much of the student's mental energy. Those who wish to study or teach scientific German for a *reading* acquaintance will find their efforts skilfully, systematically supported here. There are no bombastic claims of "German made easy"; student toil and the need for guiding it are assumed. Sequence of topics is adapted to this purpose, not to conformity with conventional German grammars. Any heresy herein will cause no pain to students, who neither know nor love the conventions.

Since some concept of pronunciation is needed even in silent reading, the first brief chapter (2 pages) is on pronunciation. Chapter 2 dives directly into the fundamentals of grammar and syntax. Copious use of illustrative examples and practice passages guides the student in applying the principles as he learns them. Exercises are mainly German-to-English (students providing the English), with just enough of the reverse to sharpen acquired skills. Analogies with English, and the evolutionary changes underlying them, are pointed out, with due warning that analogies must not be overworked. A cogent example is that *Segel* evolved into *sail*, but *Regel* evolved into *rule*, not *rail*.

Part I, in 40 chapters (160 sections), covers the grammatical instruction, with some selected from illustrative contemporary literature. Conscientious study of Part I will prepare students for facile reading of Part II (Readings in Chemistry) or Part III (Readings in Physics), all selected from modern German literature. Chemists may go on to Part III, and physicists may dip into Part II, with benefit to their reading facility. The separation is for convenience, not for segregation.

Only faint glimmers of evidence support the authors' statement that their native language is German; none reveal that they live north of the Canadian border. Their English is American, and too well written to give more than an occasional hint of their linguistic origin.

Printing and binding are praiseworthy. Layout of chapters and sections is helpful. Typographical changes (bold face, italics, asterisks before separable verbs, and footnotes) are rung in skilfully to permit maximum concentration on subject matter with minimum effort in following the arrangement.

Viewed against the prevailing book market, the price is not excessive. Viewed against the hours saved as compared with acquiring equal reading skill from books or courses less concentrated on that goal, the price out-bargains basement sales.

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Progress in Nuclear Energy Series V: Metallurgy and Fuels. Volume 2

Edited by *H. M. Finniston*, Harwell, and *J. P. Howe*, Canoga Park, California. Pergamon Press, New York, 1959. ix + 653 + xii pp. Many figs. and tables. 16.5 × 23.5 cm. $21.

A tyro in nuclear science can easily become bewildered by the profusion of publications that have been issued by the U. S. Atomic Energy Commission, by the United Nations, and others, seemingly on the same topics. There is the voluminous National Nuclear Energy Series of the USAEC, published for the Commission by McGraw-Hill Book Company, that includes among other sources the declassified documents of the Manhattan Project. Based on the 1955 and 1958 *International Conferences on the Peaceful Uses of Atomic Energy*, held in Geneva, Switzerland, the United Nations has published the many-volumed official *Proceedings*, which contain the individual papers that were presented, together with the discussions. None of these gives a broad survey of the many topics covered. Following the 1955 Geneva Conference, an eight-volume series entitled "Progress in Nuclear Energy" or the international review series in atomic energy, was published by Pergamon Press in London and by McGraw-Hill in the United States. The papers in these volumes have been selected, edited, and coordinated by experts in each field, resulting in much more comprehensive reviews than the individual papers in the previously mentioned collections. Series V is entitled "Metallurgy and Fuels," and Volume 1 in this series (1956) was largely based upon the papers given at the 1955 Geneva Conference. Volume 2, the subject of the present review, attempts to consolidate, in 41 articles, work in the field of metallurgy and fuels up to the end of 1957, and is based more on recent technical publications and reports than on the 1955 Geneva Conference papers. Volume 3, which will be published soon, will consist of edited papers pertinent to Series V that were accepted for the second Geneva Conference.

Volume 2 encompasses the same general fields as Volume 1. The numbers that are printed in parentheses in the following list show the count of separate reviews in Volumes 1 and 2 respectively, on each of these topics: uranium metallurgy (7,4), thorium and its metallurgy (2,4), magnesium (0,1), metallurgy of plutonium (1,2), zirconium (1,4), beryllium (2,3), rare earth metals (1,0), reactor control materials (0,1), ceramics (2,2), fuel elements and their fabrication (5,7), effects of radiations on materials (5,5), and solid state physics (6,8). The reviews in Volume 2 show the improvements in technology accomplished in the three-year period between the Geneva conferences. In Volume 1, for example, there are two papers on the electrodeposition of uranium metal from fused salts; in Volume 2, there is still a third review of this same topic that reveals important reductions in contamination in the deposited metal, achieved by techniques that are improvements over those reported in Volume 1. The second volume, thus, supplements the first, rather than supplanting it. Zone melting, as a method of purifying uranium, is discussed in detail in Volume 2, but does not appear to be mentioned in Volume 1, and so it goes. The historical and earlier techniques were recorded in Volume 1 and the more recent improvements in Volume 2. Volume 3 will bring these topics still further along, but again will not make the earlier volumes obsolete.

This series of edited progress reports obviously belongs in every technical library. Should the individual chemist invest in them? Probably not. He might want to have a desk copy of one or more volumes of immediate interest, but would generally not wish to possess the whole collection. Access to individual articles is accomplished through *Chemical Abstracts*, which in 1957 cited each title and author in each volume in the then existing eight series. Presumably *CA* will continue to list author and title of each contribution in the new volumes in the present twelve series. The normal literature search will soon uncover these very competent review papers on the manifold topics that now constitute the field of nuclear science.

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Colorimetric Chemical Analytical Methods

The Tintometer Limited, Salisbury, England, 1959. 360 pp. Figs. and tables. 23 × 27 cm. Loose-leaf binder. $4.20.

This fifth edition of "Colorimetric Chemical Analytical Methods" is in loose-leaf form to provide for insertion of revised and new procedures. The purchase price includes such service free for two years.

The measuring technique remains a standard series comparison, the standards in the disc or other comparimeters being Lovibond glasses selected to color match known amounts of given constituents. Each disc set is for a given desired constituent by a given colorimetric method. In the Tintometer all possible combinations of the three series of glasses may be used for color matching an object.

The contents follow: Part 1, Lovibond apparatus; Part 2, *p*H; Part 3, Inorganic constituents (25, by 47 methods); Part 4, Organic constituents (19); Part 5, Pathological constituents (41, by 46 methods); Part 6, Noxious vapors (12); Part 7, Color grading.

This comparimetric technique of measurement is very simple, and the apparatus comparatively cheap. One does need a different set of glasses for each different constituent, and the unknown must be prepared according to the procedure used for selection of the standard glasses. If one has to make only a small number of different determinations, such as *p*H, iron, and residual chlorine in water, such glasses are probably satisfactory for most situations.

Because spectrophotometers are now so generally available, and so easily adaptable, it seems likely that more and more they will be favored over comparison methods, at least in this country.

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Polymers and Resins

Brage Golding, Director of Research, Lilly Varnish Company. D. Van Nostrand Co., Inc., Princeton, New Jersey, 1959. viii + 744 pp. Figs. 16 × 23.5 cm. $12.50.

This book serves as a link between the theory and the applications of high polymer chemistry. In some ways it is a modernized version of the chemical engineering textbook on high polymers by Schmidt and Marlies, published in 1948.

The first five chapters contain a lucid summary of elementary polymer theory. Included also are comparisons of the mechanical and electrical properties of plastics. A much later chapter on the relation between molecular structure and mechanical properties might also have been included in the theoretical section.

The next four chapters are concerned with the technology of manufacture. First there are the naturally occurring polymers (cotton, natural rubber, and others), then the modified natural products (as rayons, regenerated proteins) then the condensation polymers (phenoplasts, nylon, etc.) and finally the synthetic addition products (as polystyrene and polyethylene). There are numerous good flow sheets describing the steps from the raw materials to the final polymer. Of questionable usefulness are the very detailed flow sheets for the syntheses of certain monomers reprinted from the journal *Petroleum Refiner*. These figures sometimes contain numbered parts which are not discussed in the text.

There is a chapter on fabricating and processing which includes such items as molding, extruding, spinning, and coating operations. This is then followed by a chapter summarizing the various uses for plastics.

Throughout, the treatment is up to date and is sound in the presentation of theory. Such recent topics as stereospecific polymers and block and graft copolymers are considered. It is further obvious that the author has drawn on an extremely large number of sources to obtain material for the practical sections in the book. Certainly anyone who wishes to get an overall picture of the applied polymer field could benefit enormously from reading this book. Students in chemical engineering will also find this book useful, although the high price detracts from its use as a classroom text.

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Syntheses of Heterocyclic Compounds. Volumes 1 and 2

Edited by *A. L. Mndzhoian*. Translated from the Russian by *A. E. Stubbs*. Consultants Bureau, Inc., New York, 1959. 84 pp. Figs. 15.5 × 23.5 cm. $6.

In the preface to these volumes, Dr. Mndzhoian cites the need for preparative information on the syntheses of heterocyclic compounds. To fill this need, the Institute of Fine Organic Chemistry of the Academy of Sciences of the Armenian SSR has initiated the publication of what is to be a continuing series of volumes devoted to this subject. It is pointed out that for reasons connected with the national economy, furane chemistry is extremely important and because of this, these initial volumes have been confined to this area. They contain detailed procedures for the preparation of some sixty furane derivatives so interrelated that, given enough corn cobs and a few simple chemicals, one could work his way through the entire group. It is understandable but unfortunate that none of the preparations (except that of furfural itself) involves the construction of the furane nucleus.

The pattern of these volumes is intentionally and precisely that of "Organic Syntheses" including the familiar "proposed by," "checked by," notes, other methods of preparation, and literature cited. The literature seems complete through 1954 as claimed, and the reviewer detected several references of 1957 vintage. The publishers of the translation have appended an index containing names of compounds prepared and entries such as acylation, Cannizzaro reaction, chloromethylation, Claisen-Schmidt condensation, decarboxylation, esterification, Friedel-Crafts reaction, Grignard reaction, hydrogenation, Knoevenagel reaction, lithium aluminum hydride, replacement reactions, and Wallach reaction. In general the procedures are straightforward and the techniques seem good although the reviewer feels that the use of ethyl acetate for destruction of excess lithium aluminum hydride is probably better, though admittedly less spectacular, than that of water. Incidentally, the preparation of lithium aluminum hydride is described.

While five of the preparations are to be found in essentially unchanged form in Organic Syntheses and many others are (in the reviewers opinion) adequately described in the literature, and while a few of the preparations are so simple that one questions the necessity of treating them in so detailed a fashion (the saponification of methyl 5-methyl-2-furoate, the interaction of furoic acid with thionyl chloride or of phenylmagnesium bromide with furfural, for example), some twenty-four of the compounds prepared have been described only in recent issues of *Doklady Akad. Nauk. Arm. SSR*. The book seems to be inexpensively but sturdily bound and the reviewer was able to detect no errors in the writing.

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The Chemistry of Heredity

Stephan Zamenhof, College of Physicians and Surgeons, Columbia University, New York. Charles C Thomas, Publisher, Springfield, Illinois, 1959. xii + 106 pp. Figs. and tables. 14.5 × 22 cm. $4.25.

This is a popular explanation of the present status of the chemical basis for heredity. Professor Zamenhof explains the fundamentals without delving too deeply into either genetics or organic chemistry. He emphasizes reported results and conclusions and he creates a comprehensive picture of the overall mechanism by bringing together pertinent concepts from genetics, medicine, microbiology, biochemistry, and biophysics.

The chapter titles include: Mechanisms of Heredity, Heredity Determinants as Chemical Substances, The Nucleic Acids, Mutation, Intermediary System and Cytoplasmic Inheritance, The Peripheral Reactions, and Heredity Defects in Man. A bibliography containing 185 references is included.

To this reviewer, an organic chemist, the book is a fascinating, readily-comprehensible, thought-provoking account of the progress which life scientists have made in attacking one of the most perplexing problems of science. Chemists of every persuasion will find this a thrilling, informative, and brief report.

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Great Experiments in Physics

Edited by *Morris H. Shamos*, Washington Square College, New York University. Henry Holt and Co., New York, 1959. viii + 370 pp. Figs. 17 × 24 cm. $4.40.

This book is essentially a reprinting of the original papers for 19 historically basic experiments and 5 equally basic theories of physics. It includes nearly 30 illustrations, several of which are from original sources. A modern thread thoughtfully holds the collection together by means of editorial continuity which defines obsolete words, gives explanatory notes and many items of interest contemporary with the original work as well as with the present.

Following the introduction, which contains a refreshing view of the history of science, one finds the names of those who designed the pillars of modern science through experiment and theory—Galileo, Boyle, Newton, Fresnel, Faraday, Roentgen, Einstein, Millican, Bohr, and Planck, to mention a few. Each experiment is preceded with a short biographical sketch of the worker in which the editor reveals a warm appreciation of human nature. The original description of the experiment is amply illuminated by marginal notes that clarify and modernize its meaning. The appendix deals in a similar fashion with five basic theories—electromagnetic field, quantum hypothesis, relativity, the Bohr atom, and the Compton effect. Supplementary readings are suggested for further examination of each experiment and theory.

This book provides a ready reference to the original descriptions of outstanding historical experiments in physics. Because of the collateral historical material and editorial notes, this book merits consideration for the limited library, as well as for student use in connection with courses in scientific literature and history. It is well bound and produced in a pleasing, readable format that makes for enjoyable and instructive "outside" reading.

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Principles of Dairy Chemistry

Robert Jenness, University of Minnesota, and *Stuart Patton*, Pennsylvania State University. John Wiley & Sons, Inc., New York, 1959. viii + 446 pp. Figs. and tables. 15.5 × 23.5 cm. $8.75.

"Principles of Dairy Chemistry" is a textbook in which an attempt has been made to "interpret and integrate widely scattered data in the dairy field with basic principles of chemistry."

Details of methods and technology are omitted or dealt with lightly if thorough coverage is to be found in other texts. References to these are provided. Controversial subjects are handled in such a way as to invite further inquiry, with numerous well chosen citations included.

Variations in milk composition are related to the physiology of the cow, feed, management, and other environmental factors.

The chapter on nutritive value of milk is appropriately included; nutrient composition is closely related to the chemical and physical properties of milk, and the student of dairy chemistry needs orientation in the field of nutrition. The inclusion in the appendix of the Recommended Dietary Allowances, Revised 1958, published by the Food and Nutrition Board of the National Research Council and also the Summary of Information on the Vitamins, further emphasizes the close relation between milk chemistry and the value of milk as a food.

The list of chapter headings gives an idea of the scope of this book: The Composition of Milk, Lipids, Lactose, Proteins, Salts, Enzymes, Miscellaneous Substances, Physical Properties, The Physical Chemistry of Milk Fat Globules, Physical Chemistry of the Caseinate-Phosphate Particles, The Effects of Heat, Flavors and Off-Flavors, Nutritive Value, Recommended Dietary Allowances, Revised 1958, and Summary of Information on the Vitamins.

In the opinion of the reviewer this book will be welcomed and found most helpful by both students and teachers of dairy chemistry and technology.

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(*Continued on page A316*)